Materials and Technologies for Sustainable Production

Edited by
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Preface

This edition is conceptually related to sustainable development issues.

The first book's section contains the research results in the field of wide utilisation of bio-based materials and technological processes for their processing.

There are also presented many studies devoted to waste and wastewater processing technologies, biomass waste utilisation, and improvement of soil fertility. These important problems of ecological safety are represented in a separate section.

This edition will be useful and interesting for specialists and engineers-technologists from many branches of the production sector whose activity is related to the application of bio-based materials, ecological safety, and environmental protection.

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Properties and Processing Technologies Analysis of Bio-Based Materials

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Valuation of Palm Fibers in the Formulation of Prefabricated Concrete in Southern Algeria

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Keywords: Date Palm fibers, Cementitious composites, Prefabrication, Mechanical properties, Durability.

Abstract. Algeria has known various models of construction. The general observation is the failure of construction models used not only for their inability to meet the growing demand for housing, but also for the destruction of the architectural and urban landscape. Considering the ability of natural fibers improve the mechanical properties and durability of concrete, a renewable resource and permanently available. To this end, researchers have started to search for the most durable materials that respect the environment. The objective of this research is the study of the effect of date palm fibers in cementitious compositions with various proportions on the mechanical characteristics of prefabricated concretes in southern Algeria.

1. Introduction

Algeria is rich in natural resources and in particular vegetation, the natural fibers of palm trees are a wealth for the interest of farmers, operators and industrialists. Knowing that Algeria has more than ten million date palm trees. Thanks to their advantageous mechanical properties, their possibility of recycling and their low production cost, composites with reinforcement of vegetable fibers are of particular interest to manufacturers. Concrete is a material that has become essential over time, in particular thanks to its high compressive strength, but low in traction. Indeed, traction is not really the preferred field of application of concrete. The date palm is a family of trees that produces dates, is a species whose structure is different in properties to palm wood [1] and [2]. Indeed, the palm tree is a giant grass 20 to 30 m in height, with a cylindrical trunk (the stipe), carrying a crown of pinnate leaves, divided with a length of 4 to 7 m [3](Fig1). Much research has been done on the possibility of using vegetable waste in concrete, as a replacement for aggregates, cement and for fiber reinforcement. The improvement of the durability of the plant fiber in concrete entails the treatment of the fiber or the modification of the cementitious composition [4]. The presence of natural fibers increases resistance to cracking, their post-cracking performance and toughness, and durability problems in alkaline media [5]. The surface fiber of the male date palm exhibits excellent tensile strength in concrete and mortar formulations, the authors justified their choice by saying that these fibers appear to be the most suitable to exploit [6].

Fig. 1: Date palm surface fiber

The characterization of a new concrete formulated from a base cement matrix in which the concrete mixture is reinforced by date palm fibers. Their use in the building sector can improve the thermal insulation performance of buildings, which wastes energy, without causing pollution or affecting the health of ecosystems (asbestos fibers) [7]. According to previous studies, the percentage of 0.4% and the length of 7 cm of palm fiber to be used in concrete are ideal for use in concrete [8, 9]. Previous studies carried out by Charlet have shown a link between the diameter of the palm fiber and the mechanical characteristics [10]. Indeed, the modulus of elasticity and the breaking stress are inversely proportional with the diameter of the fiber. The dosages and lengths of the fibers depend on the intrinsic parameters of the type of fiber and the mode of treatment. Other authors have studied the reinforcement of a cement paste with coconut fibers and find an optimal improvement in properties for a volume dosage of 4% and a fiber length of 38 mm [11]. Kriker [6] in his study found a decrease in compressive strength with increasing dosage and fiber length. The strength of concrete with 2% fibers (15 mm long) represents 90% of that of concrete, while that of concrete with 3% fibers (60 mm length) does not represent than about 55% of that of concrete alone.

2. Experimental Procedures

Presenting us the study materials, the concrete formulation and preparation of the test specimens

2.1 Materials used

Cement used is a CEM II class 42.5 R from the Biskra cement plant, the water is drinking tap water, the sand 0/5 mm from the river in the region, fineness modulus = 2.82 (sand is suitable for a satisfactory workability and resistance with limited risk of segregation). The fraction of the crushed stone used is (7/15 and 15/25 mm) from the region of Ain-Touta (Batna). Bulk density = 1330 kg/m^3, specific density = 2810 kg/m^3 and Los Angeles coefficient = 20% (hard). The grain size curves of the sand and gravel are shown in figure 2 and figure 3 respectively.

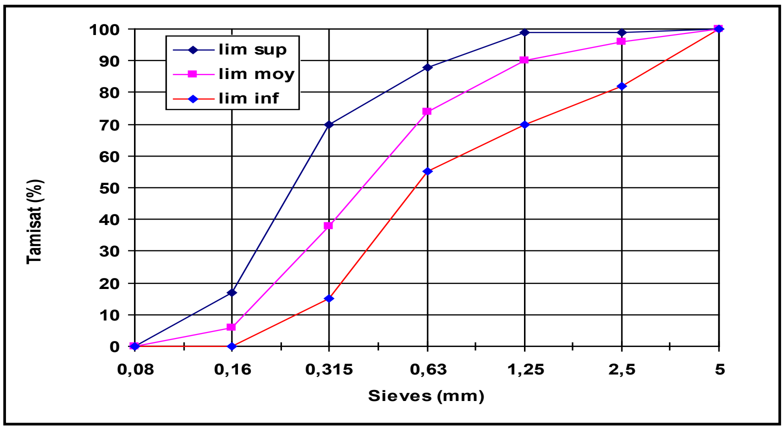

Fig. 2: Grain size curve of sand

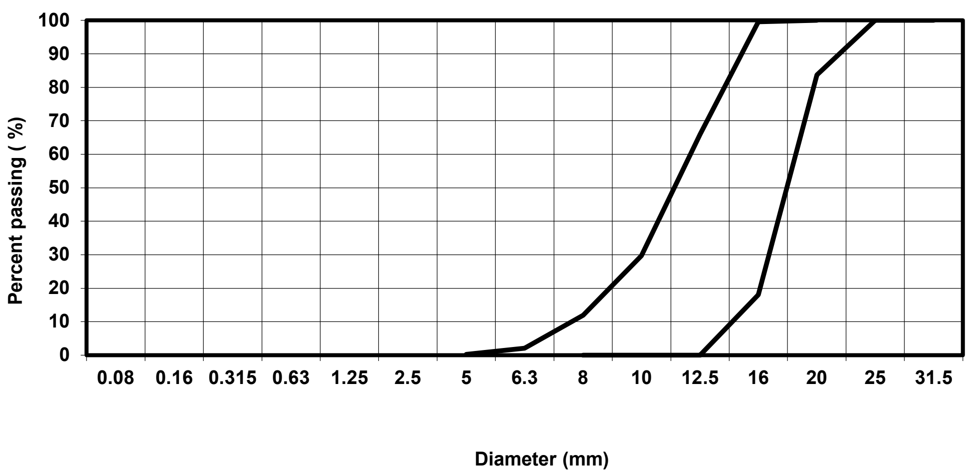

Fig. 3: Grain size curve of gravel

The physical properties of fibers

Fibers were used whose physical properties are presented as follows: diameters from 0.04 to 1mm, specific density is 0.76, bulk density is 570 kg/m^3, tensile strength is 96 MPa and water absorption is 95% of fiber was determined in accordance with standards NF EN ISO 5079.

The fiber platelets are separated into individual fibers in a tub of water to facilitate their defibration, washed with water to remove impurities, and then cut to lengths of 50 to 70 mm ± 1 mm (figure 4).

Fig. 4: Preparation of date palm fibers

2.2 Formulation of fiber concrete

This experimentation is essential to characterize the formulation campaign carried out to characterize these concretes, conservation of specimens and the mechanical test methods.
The choice of concrete formulation is based on several criteria: consistency, strength, durability and economy of concrete.

03 series of fiber-reinforced concrete are prepared for each series of lengths of 50, 60 and 70 mm, the dosage by mass of 0.5, 1.5 and 2.5% is varied, and 9 variations of fiber mixtures incorporated in the concrete are obtained (10 formulations of fiber-reinforced concrete). The water/cement ratio chosen for a slump of 80 mm ± 1 mm is (W/C = 0.55) the composition of the concrete mixes is indicated in table 1.

Table 1: Composition of concrete (kg/m^3)

Beam	B-0.5	B-1.5	B-2.5	B-0.5	B-1.5	B-2.5	B-0.5	B-1.5	B-2.5
Fiber Length (cm)	5	5	5	6	6	6	7	7	7
Fiber (% by mass)	0.5	1.5	2.5	0.5	1.5	2.5	0.5	1.5	2.5
Cement (kg)	400								
Water (L)	260								
Sand (kg)	740								
Fine aggregate (kg)	419								
Course aggregate (kg)	563								

2.3 Concrete prefabrication

Today, the modern world demands to produce concrete for construction faster and cheaper. Today's building materials are compatible with the demands of industrial production. In order to accelerate the hardening of concrete (MDPSF), heat treatments occupy an important place among the various possible methods of precast concrete. Low pressure steaming in climatic chambers is the most widely used thermal maturation means which costs nothing other than solar energy which is available in our region of southern Algeria and the other means is the acceleration of electric energy concrete hardening (MDPSF) for the precast concrete industry (MDPSF) [12].

2.4 Preparation of specimens

After mixing the concrete, the specimens are covered in plastic to prevent evaporation of water from the concrete for 24 hours. After demolding, the specimens are introduced into the steaming chamber by solar energy for one day, the specimen are retired from the chamber for drying them 3 days in the open air. Cubic (10×10×10) cm^3 samples were made to determine compressive strength and prismatic (10×10×40) cm^3 samples to determine flexural strength at one day of steaming in the enclosure (figure 6) by solar energy and 3 days in the open air (equivalent to the hardening of concrete in the open air at 28 days) . The concrete stored at an ambient temperature of 20±1 °c. (See samples in figure 5). [12]

Fig. 5: The steaming chamber and the concrete specimens

3. Results and Interpretations

3.1 Compressive strength

Figure 6 shows us that compressive strength decreases with increasing dosage and fiber length, this decrease is due to the decrease in workability by creating voids inside the concrete and that the maximum strength is that of fiber-reinforced concrete of 0.5% and 50mm in length, this increase is due to the tensile strength of the fibers and the bond between the fibers and the concrete, while the pure non-fibrous concrete has a resistance minimal compared to other concretes.

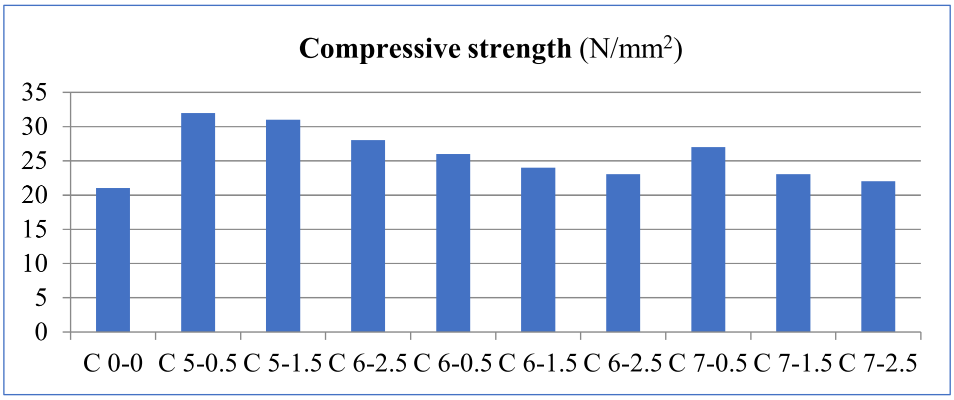

Fig. 6: Effect of fiber percentage and length on the evolution of compressive strength

3.2 Flexural strength

Figure 7 shows us the evolution of the flexural strength with the variation of the percentages and lengths of the fibers used, the resistance decreases with the increase in the length and the dosage of fibers. The 50mm fibers and the 0.5% dosage give the best strength. The flexural strength of pure concrete is the minimum flexural strength due to lack of tensile strength (no fibers) but concrete (2.5% - 7cm) is the poor flexural strength caused by an excess and rate of fibers in the concrete mix.

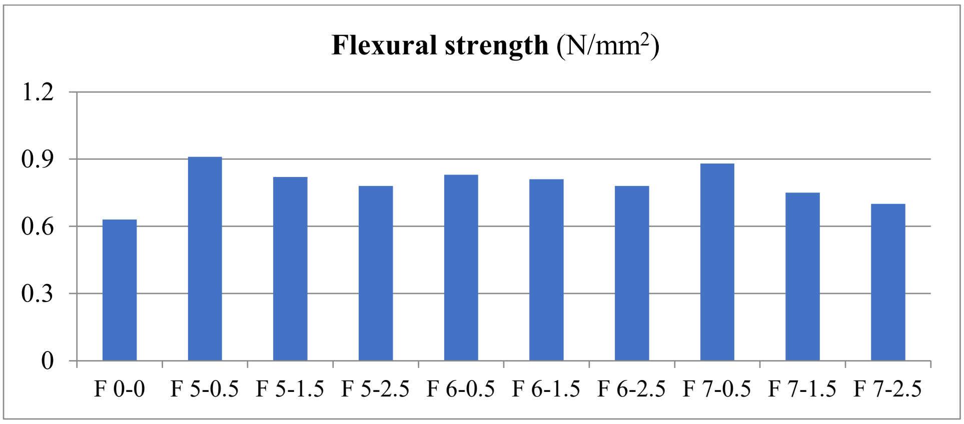

Fig. 7: Effect of percentage and length of fibers on the evolution of flexural strength

4. Conclusions and Perspectives

This experimental work shed light on research on formulations of concrete made from palm fibers and concluded with these experimental results:

1) MDPSF concrete (50mm in length and 0.5% in dosage) has the best compressive strength.

2) Observation of the fiber microstructure shows voids on the surface and that MDPSF concrete (50mm in length and 0.5% dosage) has the best flexural strength.

3) The results of this work are beneficial for further research to be developed on the accelerated hardening of palm fiber concretes by two types of solar and electric energy sources, particularly in southern Algeria.

References

[1] KARECHE, A., Etude des matériaux à base de bois de palmier dattier-durabilité, Dégradation et propriétés structurales et de transfert, Mémoire de magister, Faculté de technologie, Université El-Hadj lakhdar (Algérie), 2014.

[2] BENMANSOUR, N., Etude des performances de produits renouvelables et locaux adaptés raux applications de l'isolation thermique dans le bâtiment, Mémoire de magister, Faculté des sciences, Université El Hadj Lakhdar (Algérie), 2011.

[3] ALAOUI, S. B., Référentiel pour la Conduite Technique du palmier dattier, In "Référentiel de Conduite Technique des Principales Cultures au Maroc", Éditeurs: Si Bennasseur Alaoui et AjiroYasuhei, 2005, pp. 102-112.

[4] K.H. Mo, et al., Green concrete partially comprised of farming waste residues: a review. Journal of Cleaner Production. 117 (2016), pp. 122138.10.1016/j.jclepro.2 016.01.022

[5] J. Claramunt, et al., The hornification of vegetable fibers to improve the durability of cement mortar composites, Cement and Concrete Composites, 33(5) (2011), pp. 586-595.10.1016/j.cemconcomp.2011.03.003.

[6] A. Kriker, et al., Mechanical properties of date palm fibres and concrete reinforced with date palm fibres in hot-dry climate, Cement and Concrete Composites. 27(5) (2005), pp. 554-564.10.1016/j.cemconcomp.2004.09.015

[7] S. Abani, et al., Valorisation of Date Palm Fibres in Sahara Constructions. Energy Procedia, 74 (2015), pp. 289-293.10.1016/j.egypro.2015.07.60

[8] A. Makhroufi, Contribute to the study of the properties of palm fiber concrete in the dry and warm areas, in Department of Irrigation and Civil Engineering, 2004, Kasdi Merbah University of Ouargla.

[9] Abani, s., a. Kriker, and a. Bali, effect of curing and mix design types on performance of date palm fibres reinforcement concrete under hot dry environment, in 11th int, Inorganic- bonded fiber composites conference (iibfcc): madrid, spain, 2008, Pp. 254-259

[10] CHARLET, K., BALEY, C., MORVAN, C., JERNOT, J.P., GOMINA, M, et BREARD,J., Characteristics of Hermès flax fibres as a function of their location in the stem and properties of the derived unidirectional composites, Composites Part A: Applied Science and Manufacturing 38, 2007, pp 1912-1921.

[11] AZIZ, M. A., PARAMASIVAM, P, et S. L. LEE., Prospects for natural fibre reinforced concretes in construction, International Journal of Cement Composites and Lightweight Concrete 3, 1981, pp. 123-132.

[12] BEN AMMAR, B K., Mezghiche, B., L'effet de l'étuvage par énergie renouvelable sur la résistance à la compression des bétons, Congrès Algérien de Mécanique, 26-30 novembre, Constantine, Algérie, 2017.

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Evaluation of Environmental Impact of Palm-Fiber Based Geotextile Using a Life Cycle Method

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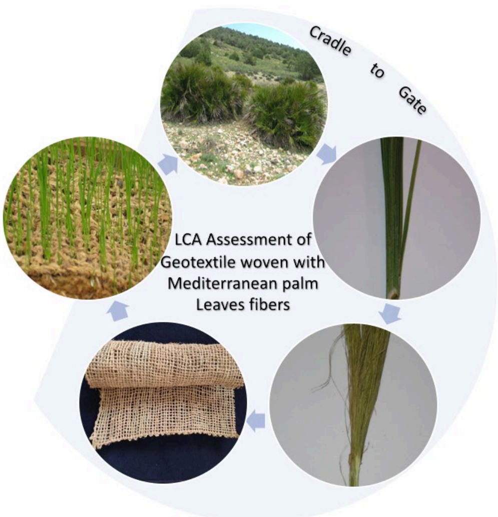
Keywords: Mediterranean palm, Palm-fiber Geotextile, petroleum-based geotextiles, Life cycle assessment (LCA), Cradle to gate, Environmental impacts.

Abstract. Currently, the geotextile industry is dominated by petroleum-based products, and the market share of bio-based geotextiles is still very low. With climatic and more generally environmental issues, combined with the scarcity of petroleum resources, the use of bio-based products appears to be an avenue of choice to explore. Through this study, we intend to raise the environmental benefits of a natural geotextile woven from fibers extracted from the leaves of the dwarf palm plant, an abundant renewable resource in Morocco and Mediterranean basin. We used the life cycle assessment analysis from cradle to factory gate following the requirements of ISO 14040 and ISO 14044 standards. Our main objective is to provide an environmental profile for this natural geotextile to encourage its use in soil protection and to stimulate therefore the local economy.
The LCA analysis results showed that the transportation phase is the main contributor to almost every environmental impact category. We also noticed that no environmental impact was identified for the raw material supply phase which is characterized by a traditional harvest of raw palm leaves from the palm plant that grows spontaneously in eco-friendly environment.
A comparison with two examples of petroleum-based geotextiles available in the market shows that palm-fiber-based geotextile presented the lower impacts in all the categories, except for eutrophication and ozone layer depletion potentials, its carbon footprint is relatively low and can save an average of 0.84 Kg CO_2 eq. per surface unit (1 m^2), nevertheless, its water consumption exceeds that recorded for synthetic geotextiles.
Finally, palm-fiber geotextile can compete with the synthetic ones used in soil erosion, it is designed from renewable resource, naturally biodegradable, requires little energy for its production, and contribute to the reduction of greenhouse gas emissions.



Introduction

All soils are naturally subject to erosion. The Food and Agriculture Organization of the United Nations (FAO) announced that 33% of the world's soil resources are degraded and in the absence of soil protection measures, the global amount of arable and productive land per person in 2050 will represent only one-fourth of the level in 1960 [1].

The use of geosynthetics and natural vegetation can reduce erosion by shielding the surface of the soil from the impact of falling precipitation, holding the soil particles in place, and decreasing the velocity of runoff [2]. Also, geosynthetics play a crucial role in road construction, they significantly improve the properties of subgrade soil [3]. Indeed, the market share of these products is constantly growing, and according to the latest report drawn up by Fortune Business Insights in 2021, the global market was valued at USD 9,014.2 million in 2020 and is projected to reach USD 16,212.5 million in 2028, However, the market share of natural geotextiles is still small, 3% compared to 93% reserved for synthetic geotextiles. 58% marketed in the world are based on straw/wood shavings, coir occupies second place with 24%, and jute with 13% market shares [4].

Although natural geotextiles are more efficient in controlling soil erosion due to their limited useful life, biodegradability, and lower cost, synthetic geotextiles dominate the market despite the disadvantages they would present related to their degradation products, we particularly quote, the microplastic particles generated under UV degradation or hydrolysis, which can cause adverse effects in the environment [4].

Because of environmental issues related to the scarcity of petroleum resources, global warming, and the principle of sustainable development which is increasingly involved in government policies, the massive use of natural geotextiles has become inevitable. Indeed, the analysis of literature and the state of technology conducted by M. Daria et al. 2020 confirmed that geotextiles made of natural fibers will be widely used in environmental engineering in the years to come [5]. To enhance this market, FAO recommended to use comparative life cycle assessment of biogeotextiles with man-made ones [6], also, D. G. Solomon, 2020, raised the need to conduct LCA of natural fibers based products to assess the reduction in CO_2 release, and to create awareness among the application of natural fiber in environmental friendly products [7].

In this study, we will attempt to throw light on the environmental benefits of using natural geotextiles by carrying out an LCA study of palm geotextile made from 100 % of fibers extracted from Mediterranean palm leaves, a very abundant plant in the Mediterranean basin. To the best of our knowledge, no studies exist on LCA of this biogeotextile, therefore, our main purpose is to provide new data on this product, to assess its environmental impact across its life-cycle from cradle to gate, and to compare the results with examples of similar synthetic products available on the market.

1. Materials and Methods

1.1. Palm-fiber-based Geotextile

Mediterranean palm, dwarf palm, fan palm, or doum (vernacular name), are all common names of the same species Chamaerops humilis L. It is characterized by low trunk, not exceeding 10 m, producing many shoots, most often remaining very short, forming large compact tufts, leaves with petiole provided with thorns on its margins, with a fan blade [8]. Widespread in the western Mediterranean region, especially in Morocco where it occupies a vast territory. It grows spontaneously in an eco-friendly environment without the need of chemical fertilizers and pesticides.

It provides income to local populations throw the sale of the palm heart (43.22 €/week/exploiter), and the marketing of artisanal products (Doum baskets: 6.2 €/week/maker) [9].

Until 1999, doum palm was exploited by nine industrial units located in morocco, for the production of vegetable horsehair obtained from the leaves fibers and used to stuff cushions, armchairs, mattresses as well as in the manufacture of woven objects such as mats, baskets, or strings [10]. Currently, doum palm has never been used as a geotextile. The samples, subject of this study, are developed by farmers, and constitute our prototypes. Our objective is to show interest of these products and to shake up this market in Morocco and abroad.

In our previous work [11], we described the manufacturing process of Palm-fiber-based geotextile which is a hand-woven product (Fig. 1) made from fibers extracted from Doum leaves harvested from Tazouta region located at 1180 m altitude in the south-east of Fez city, in the middle Atlas in Morocco. Briefly, the freshly harvested doum leaves are previously rusted and defibrated by mechanical action. The defibrated leaves are then soaked in water so that the fibers separate from the woody part and make them softer. The extracted fibers are thus braided to form a long braid fiber which will be woven to produce the doum net used as a biodegradable geotextile. Fig. 1 shows a prototype of a geotextile made from the strands of the braided fibers, it is obtained by crisscrossing the strands of the warp direction with the strands of the weft direction. Different geotextile densities can be designed depending on the density of the thread that makes up the net as well as the mesh provided during weaving. These dimensions may change depending on the mechanical and physical characteristics required.

Fig. 1: Hand-woven Palm-fiber-based geotextile (PF geotextile).

In table 1, we summarize the main features of the manufactured geotextile prototype. The sample produced is flexible and deformable which is favorable for soil stabilization, reinforcement applications, and facilitating revegetation.

Table 1: Specifications of hand-woven PF geotextile prototype.

Designation	Result
Mass per unit area [g/m^2]	1250
Mat thickness [mm]	3
Mesh size [mm x mm]	irregular (5,6 x 5,25) (mean)
Water absorbency [%]	200
Characteristics	Light and flexible

1.2. LCA methodological phases

LCA analysis is conducted following the requirements of ISO 14040 and ISO 14044 standards which define the life cycle analysis as "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle" [12].

Four steps are defined: goal and scope definition, inventory analysis, impact assessment, and results interpretation.

1.2.1 Goal and scope definition

The objective of this study is to use LCA methodology to assess the environmental impacts of biobased geotextile production using 100% palm fibers grown and transformed in morocco in comparison with conventional petroleum-based geotextiles. Our main objective is to show the environmental performance of the production process of palm fiber-based geotextile to encourage its use in the national as well as international market.

The targets of this study are geotextiles producers, farmers, ministry of agriculture, and all geotextiles users.

a. Functional unit (F.U.)

The scope of the study begins with the harvesting of raw palm leaves and ends with obtaining the woven geotextile, passing through the transport and the transformation phase of raw materials.

The functional unit selected is 1 m^2 of woven geotextile with an average mass per unit area of 1250 g/m^2 for a lifespan of 18 to 24 months.

b. System boundaries

The scope of this cradle to gate LCA study shown in Fig. 2 is limited to the production stages of Palm fiber geotextile including three phases: raw materials extraction, transportation to the factory, and manufacturing phase, and does not include environmental impact of the use and the end-of-life disposal, since the large-scale application in soil reinforcement of this prototype, has not yet been considered. Additionally, for comparison with similar products, it is assumed that natural fiber bio-based geotextiles are biodegradable and have similar lifespans and uses in soil reinforcement.

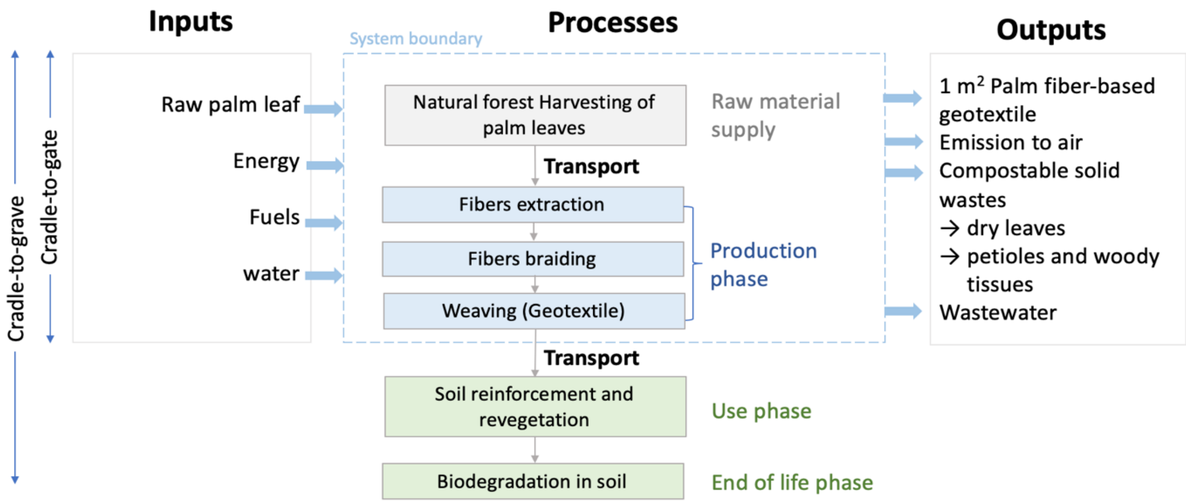


Fig. 2: System boundary of the palm fiber geotextile life cycle inventory.

1.2.2 Life cycle inventory analysis

The data was obtained from a former production site located in morocco which dates from the colonial period [10] and existing databases from Ecoinvent used in openLCA software. Table 2 shows the life cycle inventories of the production of 1 m^2 (1.25 Kg) of Palm-fiber-based geotextile.

Assumptions: The usual supply perimeters are located in several Moroccan rural communes: Bouchfâa, Smiâa, Ait Zeghrouchen, and in Rebat El Khair. We, therefore, considered the greatest distance separating the production site from these raw material collection points (100 km).

Table 2: Input and emission values related to the Palm-fiber geotextile process.

Resources / Inputs	Quantity	Unit
Raw palm leaves	2.5	[Kg]
Transportation of raw palm leaves	0.25	[t Km]
Energy / Electricity (Africa)	0.1566	[KWh]
Diesel requirement of fiber extraction	0.77	[MJ]
Water consumption	0.03834	[m^3]
Emission / Outputs		
Waste from raw leaves preparation (petioles and dry leaves)	0.5	[Kg]
Waste from fiber extraction (woody tissues and dry leaves)	0.75	[Kg]
Wastewater	0.03834	[m^3]

1.2.3 Life cycle impact assessment categories

To assess the environmental impact of palm-fiber-based geotextile, we used openLCA software version 1.10.3 developed by greenDelta in 2006 and CML-IA baseline method developed by the University of Leiden [13]. The following impacts categories are selected: global warming potential (GWP100a), acidification potential (AP), eutrophication potential (EP), human abiotic depletion (fossil fuels), photochemical oxidation (PO), ozone layer depletion (ODP), fresh water aquatic ecotoxicity (FWAE), Human toxicity (HT), terrestrial ecotoxicity (TE). Additionally, we used the cumulative energy demand (CED) method to assess the resources consumption along the life cycle of our geotextile [14].

2. Results and Interpretation

2.1 Environmental profile of Palm-fiber-based geotextile

2.1.1 Environmental impacts

Environmental impacts associated with the production of PF geotextile from cradle to gate are shown in Fig. 3.

The LCA results show that all of the impact categories are largely dominated by the transport phase except for marine aquatic ecotoxicity for which the manufacturing phase slightly exceeds transport. However, no environmental impact was detected for the raw material supply phase, this is due to the fact that during this phase, no machine inputs are considered since raw palm leaves are harvested traditionally by the villagers and the dwarf palm grows spontaneously in the middle Atlas in Morocco and all around the Mediterranean basin, benefiting from natural precipitation, and does not need any chemical fertilizers and pesticides for its growth.

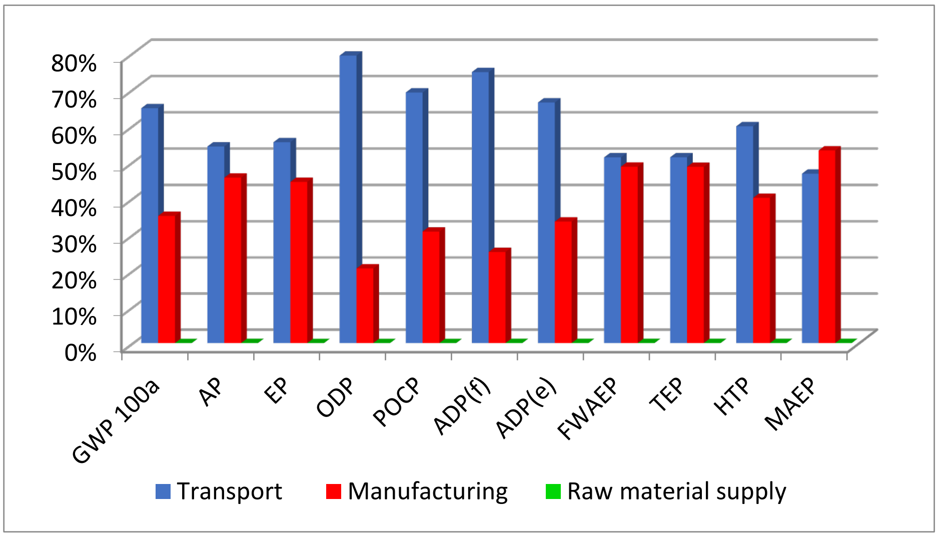


Fig. 3: Life cycle Environmental impacts from cradle to gate of 1m^2 palm fiber-based geotextile.

GWP 100a = Global Warming Potential | AP = Acidification Potential | EP = Eutrophication Potential | ODP = Ozone layer depletion Potential | POCP = Photochemical Oxidants Creation Potential | ADP(f) = Depletion of abiotic resources-fossil fuels | ADP(e) = Depletion of abiotic resources-elements | FWAEP: Fresh Water Aquatic Ecotoxicity Potential | TEP = Terrestrial Ecotoxicity Potential | HTP = Human Toxicity Potential |. MAEP = Marine Aquatic Ecotoxicity.

2.1.2 Carbon footprint

Fig. 4 represents the carbon footprint of PF geotextile for a product surface of 1 m^2 (1.25 Kg). The results show that 0.725 kg of CO_2 eq. is produced for every 1 m^2 of geotextile, and the transport phase is the principal source of GHC emissions and generates 64.83 % of CO_2 eq. The manufacture phase part was also a significant contributor to total emissions, at 35% of the total.

For the raw palm leaves supply, zero material carbon footprint value was generated, because palm leaves are a bio/renewable feedstock and are harvested manually which does not require any energy source.

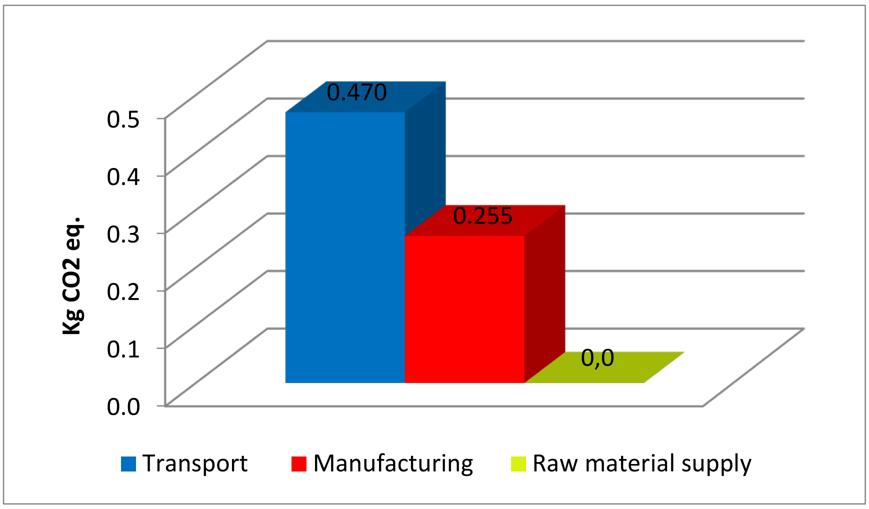


Fig. 4: Carbon footprint value for Palm-fiber-based geotextile.

According to the environmental product declaration of 1 m^2 of Secugrid made from PET, 1,9 kg CO_2 eq. is produced [15], and 1.23 kg of CO_2 eq. for the same surface area of geogrid TriAx TX 190L-G made from polypropylene [16]. A comparison of the carbon footprint of geogrids made from petroleum resources shows that PF geotextile has a lower carbon footprint impact and can save an average of 0.84 Kg CO_2 eq. per surface unit (1 m^2).

The above results show that palm-fiber-based geotextile features a significant CO_2 saving compared to conventional geotextiles, and can therefore contribute to the reduction of greenhouse gas emissions.

2.2 Palm-Fiber based geotextile vs petroleum-based geotextile

A comparison of the environmental impacts of Palm-fiber-based geotextile, polyester and polypropylene geotextiles are reported in table 3.

Palm-Fiber based geotextile shows the lower impacts in all the categories, except for eutrophication potential and ozone layer depletion potential.

Table 3: Cradle to gate environmental impact assessment of 1 square meter of geotextiles.

Environmental Impacts		Secugrid® PET (Polyester) [15]	Geogrid TriAx TX190 G (Polypropylene) [16]	Palm-fiber based geotextile (This study)
	Unit	580 [g/m^2]	434 [g/m^2]	1250 [g/m^2]
ADP(e)	[kg Sb^-eq.]	8.78E-06	2.70E-07	2.67E-06
ADP(f)	[MJ]	43.57	35.1	8.38
GWP	[kg CO_2 eq.]	1.901	1.23	0.7249
ODP	[kg CFC11 eq.]	6.43E-08	7.82E-11	9.91E-08
POCP	[kg Ethen eq.]	3.81E-04	4.14E-04	2.70E-04
AP	[kg SO^{2-}eq.]	6.10E-03	3.04E-03	3.78E-03
EP	[kg $(PO_4)^{3-}$eq.]	7.85E-04	2.91E-04	1.10E-03

We can note a reduction of 76 to 80% of fossil energy resources consumed for the production of 1 m^2 of bio-based geotextile. Greenhouse emissions of PET and PP-based geotextiles are almost twice than PF geotextile, this is due to a more energy-consuming production process.

Indeed, this result is confirmed by the analysis of the cumulative energy demand (CED) (Table 4). The global energy consumption varies from 9.5 to 49.5 MJ_{Prim}/f.u. The use of biobased geotextile allowed a reduction of 80% of energy demand, unlike the water demand which is about 80% higher using palm-fiber geotextile.

Table 4: Cumulative energy demand and water use for the production of 1 square meter of geotextile produced.

Resource use	Unit	Secugrid® PET [15]	Geogrid TriAx TX190 G [16]	Palm-fiber based geotextile (This study)
Non-renewable primary energy resources	[MJ]	48.036	37.7	9.307
Renewable primary energy resources	[MJ]	1.456	1.17	0.202
Use of net fresh water	[m^3]	4.24E-03	4.94E-03	0.039

Conclusion

The environmental impact of palm fiber-based geotextile was evaluated using a cradle-to-gate life cycle assessment. The obtained results indicate that the transportation stage is a major contributor to most of the impact categories, while the impacts associated with raw material supply can be neglected since palm leaves are harvested traditionally without the use of machinery.

Additionally, palm-fiber-based geotextile features a significant CO_2 saving compared to conventional ones, 0.84 Kg CO_2 eq. per surface unit (1 m^2) can be saved, and can therefore contribute to the reduction of greenhouse gas emissions.

The palm fiber geotextile has lower environmental impacts than those counterparts prepared from PP and polyester fibers, except for eutrophication and ozone layer depletion potentials.

A substantial reduction in energy demand was also raised for PF geotextile, the global energy consumption of 9.5 MJ per 1 m^2 which appears to be very low compared to the same surface unit of PET and PP-based geotextiles.

According to the above results, we can state that PF geotextile can be considered an eco-friendly product, its introduction into the Moroccan and international market will contribute to the socio-economic development of regions where the doum palm is abundant, and where the population strongly needs a source of income to live decently.

References

[1] Information on http://www.fao.org/news/story/en/item/270812/icode/ (accessed May 23, 2021). Food and Agriculture Organization of the United Nations (FAO), Nothing dirty here: FAO kicks off international year of soils 2015.

[2] A. Mwasha, Practical Guide to Green Technology for Ground Engineering, Rapra Technology Ltd (Ed.), Shawbury, 2011.

[3] A. Mittal and S. Shukla. Effect of Geosynthetic Reinforcement on Strength Behaviour of Weak Subgrade Soil, Mater. Sci. Forum. 969 (2019) 225-230.

[4] G. Leson, M. V. Harding, K. Dippon, Natural Fibres in Geotextiles for Soil Protection and Erosion Control, in: J. Müssig, C. Stevens (Eds.), Industrial Applications of Natural Fibres: Structure, Properties and Technical Applications, Wiley–Blackwell, Chichester, West Sussex, U.K., 2010, pp. 509-522.

[5] M. Daria, L. Krzysztof, M. Jakub, Characteristics of biodegradable textiles used in environmental engineering: A comprehensive review, J. Clean. Prod. 268 (2020) 122129.

[6] Food and Agriculture Organization of the United Nations (FAO), Unlocking the commercial potential of natural fibres, Market and policy analyses of the Non-Basic food Agricultural commodities Team, Trade and Markets Division, 2012.

[7] D. Solomon, Application of Natural Fibers in Environmental Friendly Products, Int. J. Environ. Sci. Nat. Resour. 25 (3) (2020) 147-153.

[8] A. Benabid, Flore et écosystèmes du Maroc : évaluation et préservation de la biodiversité, Ed. Kalila Wa Dimna, Rabat, 2000.

[9] N. Lachkar, F. Lamchouri, H. Toufik, Socioeconomic position of Chamaerops humilis L. var. argentea Andre in the province of Taza (North East Morocco) and impact of the new Moroccan law n° 77-15 (Moroccan Official Bulletin N° 6422) on the preservation of the environment, Ethnobot. Res. Appl. 20 (2020) 1–14.

[10] R. Sammoudi, Diagnostic de l’état actuel de la vannerie à base d’Alfa et du palmier nain dans la province de Taza et perspectives de valorization, Doctoral thesis, Ecole Nationale Forestière d’Ingénieurs, 1999.

[11] L. Laasri, WO Patent 2010137931A2 (2010).

[12] Information on https://www.iso.org/obp/ui/#iso:std:iso:14040:ed-2:v1:en (accessed April 25, 2021). ISO 14040:2006, Environmental management - Life cycle assessment - Principles and framework.

[13] CML - Department of Industrial Ecology, CML-IA Characterisation Factors, Leiden University, 2016.

[14] R. Hischier, B. Weidema, H.-J. Althaus, C. Bauer, G. Doka, R. Dones, R. Frischknecht, S. Hellweg, S. Humbert, N. Jungbluth, T. Köllner, Y. Loerincik, M. Margni, T. Nemecek, Implementation of Life Cycle Impact Assessment Methods - Ecoinvent Report No. 3 v2.2, Swiss Centre for Life Cycle Inventories, Dubendörf, 2010.

[15] NAUE GmbH & Co. KG, Environmental Product Declaration (EPD) Secugrid®, Germany, 2017.

[16] Tensar International Limited, Environmental Product Declaration (EPD) - Geogrid TriAx TX 190L-G, United Kingdom, 2017.

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Date Palm Industrial Benefits and Secondary Metabolites Production by Biotechnology Approach

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Abstract. Date palm (*Phoenix dactylifera* L.), commonly grown in the hot arid zones predominantly in the Middle East and North Africa, became one of the highly important cultivated palms around the world, because of the multiple processing utilization of the edible fruit, and the various industry- uses of the whole tree parts. Moreover, there are intensive studies indicated the higher nutraceutical value of the essential biological compounds in the date palm tissues like (carotenoids, phenols, lignin, flavonoids, tannins and sterols) and their therapeutic aspects, such as antioxidants (lutein, β-carotene and vitamin A), antibacterial (syringic acid, vanillic acid and gallic acid), antifungal (tannic acid) and anti-cancer (quercetin) and anti-sterility (β-sitosterol and stigmasterol). Meanwhile, the biotechnology approach provides the production possibilities of the plants' secondary metabolites, using cell suspension cultures and the scale-up by bioreactors. Also, using the biotic and abiotic elicitors as important factors inducing bioactive compounds accumulation in plants tissue cultures. This review describes the progress in studying the in vitro production of some important secondary metabolites from the date palm tissues.

Introduction

Phoenix dactylifera L. is namely date palm, as it is identified all over the world. All palm trees are tropical to sub-tropical regions. Date palm nature is a perennial tree and diploid (2n = 36). The classification of date palm tree in the plant Kingdom belongs to the Angiosperms, monocotyledonous, Arecaceae family, which consists of 200 genera. The date palm genus is called the Phoenix genus, and among more than 1500 species are related, dactylifera is the date palm species. The majority of related to the Phoenix genus are considered as ornamentals trees [1,2]. Mesopotamia zone (southern Iraq), Egypt, and western India are the suggested native places for date palm trees since ancient times [2,3,4,]. The principal cultivation regions of date palm in the world are distributed in the deserts of the Arabian Peninsula, Middle East and North Africa. Initially, date palm cultivation spread by seeds means, then through the means of the offshoots germplasm exchange the cultivation of date palm widely spread to the other parts of the world [4,5,6,7].
The botanical discretions of date palm tree showed special characteristics, being to a monocotyledon plant. The date palm tree has vertical, lignified trunk, with no ramification (lacking cambium). It is grass-like: rather flexible to strong desert winds. It is brown in color, has a cylindrical shape, and its height may reach up to 30 m at the maturity phase and ended upwards with the upper crown of moderately dense ranging of 60–80 of green leaves about (3–6 m in length). It is completely covered with the bases of all the dried old leaves fronds (rachis base), The fronds (leaves) are pinnate, with a midrib (rachis) that holds about 150 stiff leaflets (2 cm width and 30 cm length). Meanwhile, there are modified leaflets identified as sharp spines, also located at 10–15 cm on each side of the midrib base (Fig 1). Annually about twelve new leaves emerge. Every leaf has an auxiliary bud, which may be differentiated as a vegetative, floral or intermediate. The date palm roots have a special growing

features, which highly reach deeply for more than 6 m, and about 25 m from the main palm tree to the water places, Root system anatomy has a special structure as a monocotyledon, it is lacking cambium, with a fibrous in nature, it is characterized as the primary root which grows directly from its monocotyledonous, and the secondary roots appear on it, and produces, in turn, the adventitious roots. Being as dioecious plants, the date palm flowers (inflorescence strands) emerge separately on male or female trees, (Fig 2). and they are covered with a rigid fibrous cover called a spathe, that appears shorter and wider in the male spathes than the female one. In general, both female and male inflorescence has 3 sepals and 3 petals. The female flowers give the date palm fruit. The fruits shape is ovoid to oblong, have a smoothly thin fruit skin called (pericarp), and the fleshy part is called monocarp, then the endocarp part of the only elongate single seed covered by a fibrous parchment [2, 3,4,8].

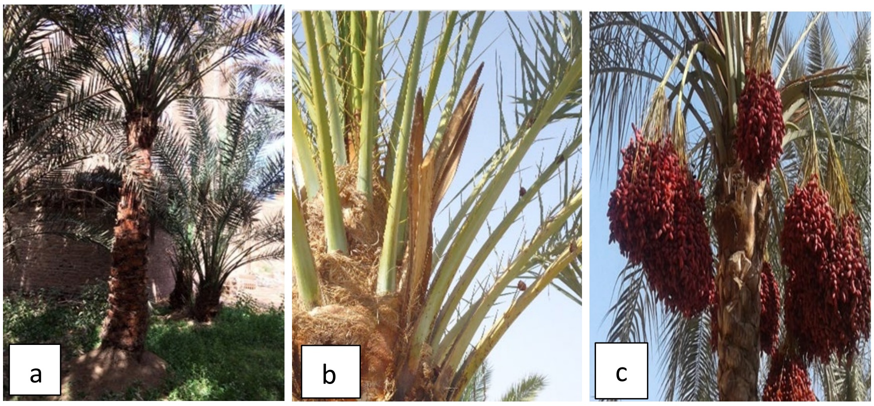

Fig. 1 The botanical discretions of date palm tree showed special characteristics, being to a monocotyledon plant. The date palm tree has vertical, lignified trunk, with no ramification, and carried the upper crown, with green leaves. The leaves are pinnate, developing upward in a spiral shape (a). The midrib of date palm frond (rachis) holds stiff leaflets, modified leaflets identified as sharp spines(b). The fruits have ovoid to oblong shape (c).

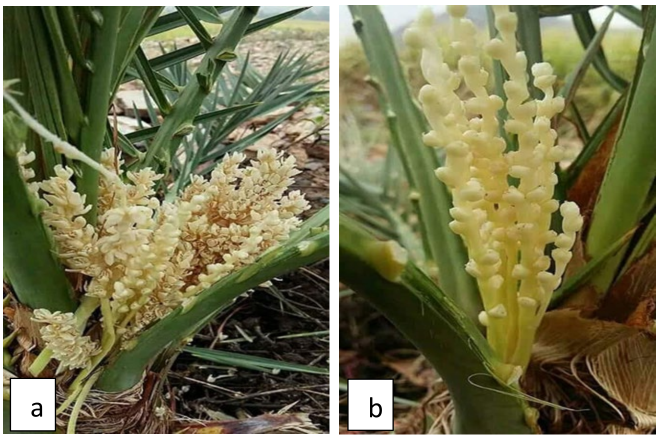

Fig. 2 The date palm is a dioeciously plant; where the (male) (a) and (female) (b) flowers are carried on two separate trees. Female flowers are typically appearing yellowish green, but the male flowers are different, they are waxy-white in appearance.

The important utilization and industry- uses. The date palm tree shows advantages being one of the most important cultivated palms around the world, besides its principal role in the economy of many countries of the Middle East and North African Zone It is true that, date palm means the "tree of life", because of the vital relation for human settlement, prosperity and nourishment security in the main regions of the date palm cultivation areas [2,6,7]

Date palm tree possesses a huge multipurpose, not only for sugary fruits and their high nutrition value but also for the additional utilization for the whole tree parts. The dates can be consumed as edible fruit or as basic raw materials components for many food products. There are many food industries depending on the fruits itself, like energy sweet bars, date pastes, jam, syrup, dates butter.

meanwhile there are food industries depending on the fruits by-products like, dates soda, energy beverages, fermented beverage, date's vinegar. On the other hand, seeds considered as dates wastes, which also, can be used as a source of food oil and it has been suggested for margarine production, whereas, the grinding powder of dates seeds used with white flour for bakery products, also, this powder has a special use as a dates coffee drinking, also, seeds powder presents a rich source of nutrition for men and for animal's feeding like cattle, horses, goats, sheep, camels and poultry [4,9,10,11,12]. Moreover, there is a special trend to produce industrial material, such as biofuels, biopolymers, antibiotics and organic acids from dates fruit by-products and seeds [13,14,15]. Generally, from the past and so far there are traditional by-products, manufactured from the different parts of the date palm tree, like rustic furniture, beams, poles, light footbridges, roofing and bags and baskets like rustic furniture, beams, poles, light footbridges, roofing and bags and baskets [1,2]. Recently there are a great interest to apply green chemistry principles for biomass utilization and waste minimization since the date palm tree annually has a great number of wastes have been estimated for about 33 Kg/tree, presented in leaves, fronds, mesh, fruit holders. The date palm fibers perform an auspicious substitutional to synthetic fibers in polymer composite industries [16,17]. Also, the processing of the date palm biomass waste to produce the bio-oil and biochar, by using the modern technology of pyrolysis equipment, are a great source, for excess bio-energy of heat and electricity, which can be used for various purposes [18,19]. Meanwhile, there are other various modern industries, produced from the date palm wastes, like wood-cement composites [20] wood-plastic composites [21]. Date palm tree as a whole is naturally renewable raw materials, which can be used in various industrial applications.

Secondary Metabolites Profile and biological activity. Date palm is rich in many secondary metabolites of biologically active phytochemical constituents, which have commercial, medicinal and poisonous properties that can be utilized [4,7,15]. The Bioactive compounds of date palm secondary metabolites can be grouped as nutritive or nonnutritive molecules. Non-nutritive bioactive molecules as phenolic acids, carotenoids, flavonoids, polyphenols and phytosterols, where the nutritive bioactive compounds such as soluble and insoluble, non-starch polysaccharides, α-tocopherols and β-carotene. ([22,23,15]. The sweet edible fruits of the date palm tree are a certain source of many important bioactive compounds [4,10,24]. However, the composition and concentrations of the bioactive compounds present in dates fruits are widely varied regarding several parameters, including the stage of fruit repining, date variety, the geographical origin of the dates and the soil conditions, postharvest processing and storage state. [10,22,15]. In general, there are high variations in the amount of the secondary metabolites in the date palm tree depending on the type of organs, where the highest levels of most bioactive compounds are present in date fruit, and the least amount can be found in the roots [25,26,15]. (El Hadrami et al. 2011) [27] reported that the highest concentration of phytosterols was in the pollen grains, while the least abundant in date fruit. In general, the phenolic acids metabolites present in date palm tissues include protocatechuic, gallic, caffeic, p-hydroxybenzoic, vanillic, ferulic, syringic, P-coumaric, and o-coumaric acid [24,7]. In general, Polyphenols constitute detected in date palms are coffee acid, kaempferol, catechin, and apigenin, whereas the most abundant polyphenols in date palms are the condensed tannins. [26,27,28]. Meanwhile, the Carotenoids presents in date palm fruit in four main groups, the most abundant one being lutein, then neoxanthin, β-carotene, and zeaxanthin are followed. In addition, α-carotene and β-zeaxanthin were found in a very small amount in the fruit at the rutab stage of some cultivars [10,22,15]. On the other hand, phytosterols are the least abundant in date fruit [21,10,15]. The most predominant phytosterol detected in date palm is β-sitosterol, additionally to other sterol compounds like stigmasterol, campestral, and isofucosterol. determined the profile of phytoestrogens content in date fruit and they found several phytoestrogens including formononetin, daidzein, genistein, glycitein, matairesinol, lariciresinol, pinoresinol, secoisolariciresinol and coumestrol [29,15]. Flavonoids are considered as a large family of polyphenolic secondary metabolites in date palm different cultivars [7]. The total content of flavonoids decreases significantly during maturity stages from the Khalal stage to the Tamer stage for different date fruits varieties [30,31]. [32] found thirteen glycoside flavonoid glycosides of apigenin, luteolin, and quercetin and flavonoid sulfates in date fruit

Deglet Noor cultivar, collected at Khalal stage of maturity. In another study on eleven different Saudi date fruit cultivars, apigenin, luteolin, quercetin, isoquercitrin, and rutin were determined [33]. In the Amari and Hallawi cultivar of date fruits, Kaempferol, a natural flavonol, were identified [34]. Anthocyanins are other substantial bioactive compounds present in date palm fruit, which were detected only in fresh fruits [35,15].

Pharmaceutical Potential. Date palm tissues have different pharmaceutical potential, due to the existence of broad quantities of bioactive compounds [2,7,15]. The ability of date extract for scavenging the free radicals could be assigned to the presence of two prime sets of antioxidant compounds, the first set is the wide range of phenolic compounds, including the different phenolic acids, flavonoids and procyanidins, and the second set is the presence of other water-soluble antioxidants, such as vitamin C and the oligo-elements [36]. The antioxidant properties of the phenolic compounds, that are present in date palm tissues, exhibit a broad range of biological effects, where the phenolic act as free radical quenchers, that prevent oxidative damage for nucleic acids, proteins and lipids in the human body. In addition to, the high potential of the phenolic on the modulation of the physiological, biochemical or molecular state of the cells [2,7,15]. So that the risk of some chronic diseases can be, prevent through date palm diet nutrition. Date fruit may possess a potential of bioactive compounds, with high antioxidant activity, for the health benefits against a number of cancer types and cardiovascular diseases [7]. It was reported that consumption of date fruits might induce health state of the colon by increasing the growth of beneficial bacterial and inhibiting the proliferation of colon cancer cells [37]. Also, the activity of specific compounds like flavonoid glucosides (quercetin), which are known by their cancer chemoprotective features were studied in parthenocarpic dates extracts [38,39]. In this context, it was demonstrated that the P. *dactylifera* dates have special therapeutic effects in the prevention of cancer, due to the higher existence of the components of the antioxidant of polyphenolic compounds. [40].
Other therapeutic effects of date palm extracts, appeared as antidiabetic and in the prevention of pathological parameters of diabetic neuropathy. [41]. In addition, Pujari et al. 2011 [42], determined the significant effect of dates contents on the protection of the nervous system against cerebral ischemia, caused by the arteries occlusion disease. Garba and Galadima 2012 [43], showed the significant activity of the dates extracts as anti-diarrhea for its antimicrobial property against the bacteria, salmonella spp. and *Shigella* spp, which causes diarrhea disease. Recently, (Belmir et al. 2016) [44], studied the antifungal activity of date fruit extract of cv. Ajwa at Tamr stage with the amphotericin B (an antifungal drug), they found that therapeutic activity of amphotericin B has been induced significantly with the addition of date extract, moreover, the aqueous date extract prevents cytotoxicity of red blood cells induced by the test of amphotericin B.

Also there is an important therapeutic effect of date palm pollen grains, well recognized to be as an anti-sterility agent, which considered as an excellent source of phytosterols, like ß-sitosterol and stigmasterol [45,15]. Reported that the chemical compounds accumulated in date palm, are not only limited to the benefits to humans as bioactive compounds but also can be responsible for the pest and pathogen resistance in the plant host [15].

In Vitro Production of Secondary Metabolites

Secondary metabolites biomass Accumulation. In general, most plant biomass substrates, utilized for several benefits and commercials uses in human life, such as nutraceuticals, pharmaceuticals, construction materials and bioenergy sources. Bioactive compounds derived from different secondary metabolites pathways in plant cells are considered one of the most important resources of plant biomass for the pharmaceuticals industry [46]. Secondary metabolites, accumulation in the plant biomass as chemical compounds without a clear biochemical role in building, and development during the plant life cycle [47]. Numerous, secondary metabolites (SMs), are of important four major groups phenols, alkaloids, glycoside and terpenes, produced to serve a variety of physiological defense processes, against external environmental stress conditions of temperature, light, humidity, and pathogens attack [48,49]. The secondary metabolites often accumulate in the plant in specialized cells or organs, and their production is often low (less than 1% DW) and it depends greatly on plant species and plant's physiological and developmental stage [50,51]. Many studies showed evidence implicit the stress conditions as signals to increase secondary metabolites accumulation in the plant biomass [52,53]. The enhancement of secondary metabolites accumulation in the plant biomass, through using molecules of biological and non-biological origin (microbial, physical and chemical) of different stress factors as elicitors, to obtain the valuable bioactive compounds is known as the elicitation process [54,55]. Recently, the progress in molecular biology, enzymes, physiology, and the different basic biotechnological processes, of plant cultures suggest that the in vitro cell cultures become a viable source of important plants bioactive compounds production [56,50,57,58,59]. Therefore, using tissue culture technology gave an attractive alternatives opportunity for the production of date palm secondary metabolites biomass.

Secondary Metabolites Production in Cell Suspension. Cell suspension culture has a great immediate capability of the industrial applications due to production, and isolation, of the phytochemical compounds, can be more rapid, simpler, and more predictable as compared to, the complex traditional extraction from the whole plant [51]. Moreover, cell suspension culture eliminates the issue of the interfering of plant compounds that are appeared in field-grown production. Hence, important secondary metabolites can be produced widely under optimized and controlled environment conditions, connected with high-growth cell line selection, for the production of the required metabolites [60]. Cells in suspension can exhibit higher rates of cell division acceleration than the cells division in the callus culture. Thus, cell suspension offers advantages when rapid cell division or many cell generations are desired [50]. However, Cell suspension culture is formed by the agitation, of the introduced friable callus tissues into a liquid nutrient medium. These agitated cells are highly divided, besides having the totipotent potential of synthesizing any of the compounds, which are normally contained in the plant source [61]. In this system, nutrient components of the basal liquid media are the key, employed for the production, of most plant secondary metabolites [62]. where, the optimum nutrient concentration of culture media type, and the type and concentration of the growth regulators, are critical determinant in the accumulation of the different secondary metabolites [62,63]. In the date palm callus culture, the accumulation of the steroids and the total phenols were significantly affected by the salt strength of (MS) medium and the microelements concentration [64]. In addition, the pH, the premier size of the inoculum and cell aggregate play intrinsic roles in the initiation and production of secondary metabolites in cell suspension cultures, through optimizing the enzyme activities as well as gene expression [65,66]. The optimum biomass accumulation, of established cell suspension cultures, is determined by the growth curve for packed cell volume as well as fresh and dry weights [67]. Clearly, in the exponential growth curve, the production of most secondary metabolites is obtained during the plateau (Stationary phase). Where, in the early stages of the growth curve, lack of production is occurred, due to primary metabolism for the building of cells structures and the respiration processes [68,69]. On the other hand, secondary compounds are more actively synthesized, when growth stops and no longer needed for carbon, in large quantities for the primary metabolism. Many new enzymatic activities appear during this plateau phase, a frequently observed absent, during lag or, log phases [60,70]. Many authors demonstrated the possibility of biochemical differentiation of the cells when the cell growth is stopped. However, some secondary plant products such as battalions and carotenoids are known to be growth-correlating with undifferentiated cells [70]. Plant cell suspension culture technique is largely reported in many plant species for the production of vast important bioactive compounds for pharmaceutical applications [71,72,66,73]. Limited studies were carried out in the date palm cell suspension cultures for some bioactive compounds.(EL-Sharabasy 2000, 2004) [45,74], studied as pioneer the possibility of the production of the steroids from embryonic callus of some Egyptian varieties of the date palm, by using the cell suspension cultures. Taha et al. 2010 [75], studied the production of phenolic and peroxides compounds in suspension cultures of Egyptian varieties of date palm. Recently, (Naik and Al-Khayri 2017, 2018) [29,69], have investigated the date palm cell growth curve in relation to the optimum production of biomass and specific polyphenol compounds, and they found that, catechin, caffeic acid, apigenin and kaempferol were produced at optimum level from the cell suspension cultures of date palm after the 11th and 12th weeks of culture establishment. So far, no work has been done.

Secondary Metabolites Production in Bioreactors. Bioreactors performance, considered as a biological factory, for inducing and producing, high quality of vital secondary metabolites. The field of metabolic engineering of medicinal plants endeavors to create a true manufacturing industry based on the bio production of commodity chemicals in cell factories by bioreactors technology. The large requirement amount of biomass production, lead to bioreactors being a convenient alternative to ordinary plant tissue culture protocols. [76]. The principal advantages of using this technique appeared in, renewal supply, suitability for high scaling-up of cell suspensions cultures productivity, increase the homogeneity of the culture appearance, due to the stirring mechanism, enhancing nutrient uptake, enable of controlling the cultural growth parameters, such as, nutrient media, pH, temperature, etc., which stimulates the cell division rates, and yield a high concentration of bioactive compounds. Also, simpler and faster cells harvest and easier separation of the target compounds, because of the lower complexity of the extraction method. Moreover, opening the opportunity of performing the biosynthesis, and/or biotransformation experiments relating to the metabolite production with the enzymes. [77,58]. The achievement for the main production of estimated and valuable chemical components by the plant cell and tissue cultures need the correct selection of a suitable bioreactor [77,58,76]. Where, the selection rules are determined based on many essential factors, that have limitations according to the plant cell culture and are affected by the production aims. It is clear that the optimal bioreactor system for a plant tissue culture is quite different from a plant suspension cell culture on the commercial scale. The bioreactors are classified into different designs; each one has advantages and disadvantages of their configurations. Mechanically agitated, pneumatically driven, disposable and non-agitated are the main different types of bioreactors [78,79,80]. There are different modifications of bioreactors types like (Stirred Tank Reactor, Bubble Column Reactor, Airlift Reactor, Orbital Shaken Bioreactors, Wave-Mixed Bag Bioreactor, Nutrient Mist and Nutrient Sprinkle Reactors). The most common bioreactor is the stirred tank bioreactor, which has an adequate know-how usage, in many studies of plant secondary metabolites production [78]. Optimization at the large scale of plant cells can be carried out by the chosen proper bioreactor, which is defined by the engineering parameters of the bioreactor configurations, such as the options of cell aggregation, mixing, aeration, shear sensitivity, and efficient illumination [76,81]. However, maximization of desired metabolite's productivity in the bioreactor system also can be conducted through the election of the proper precursors feeding, which are biochemical compounds that are needed as intermediary compounds of the metabolic pathway for the synthesis of desired bioactive compounds [62,82,83, 84]. Pyruvic acid at 0.01 mg L^{-1} used as precursor to induce sterol production in date palm cell suspension nutrient medium [85]. In general, the cultivation system in the bioreactor, and the extraction procedures of intracellular metabolites are very critical considerations in scaling up of plant cell cultures to bioreactors system [86]. Progress was achieved commercially for some plant bioactive compounds as alkaloid production from Vinca, Rubia dyes, shikonin from *Lithospermum erythrorhizon*, arbutin using *Catharanthus roseus*, ginsenoside-rich biomass using Ginseng root *Panax ginseng* cultures, berberine production from *Coptis japonica* and the scaling up for cell suspension cultures system for *Taxus chinensis* [58,59]. In the date palm, a serried tank bioreactor was used for micropropagation and scaling up the production of bioactive compounds [87]. It has been demonstrated that in the bioreactor system steroids synthesis was induced in the embryogenic callus of the date palm, about 14 times extra than being on the ordinary solid medium. Therefore, the date palm phytosterols as important medicinal compounds can be commercially produced by using bioreactor systems [74,85]. Although, the numerous studies and applications in this filed, delayed growth rate of plant cell cultures and the high fundamental costs implicated in cell culture techniques, represent the big challenges in the exploiting of industrial-scale bioreactors [50,62]

Elicitors factors influencing secondary metabolites in vitro accumulation

Abiotic elicitors

Radiation. Among different elicitors, light qualification or quantification are highly affected plant development, morphogenetic responses and the synthesis of the valuable bioactive compounds [88,89]. Ahmed and Baig 2014 [90], reported that using color variable lights are a promising election strategy for advocating the production of antioxidant bioactive metabolites in the callus cultures of S. *rebaudiana*.Meanwhile, In *Artemisia absinthium*, L. callus cultures, the exposure to different monochromatic lights resulted in a significant variation both in the morphogenic structure and in the biochemical contents. [89]. The blue light effectively increased the phenolic and the flavonoid contents than the control in the callus cultures of *Stevia rebaudiana* [91]. Also, the scopoletin production in cell suspension cultures of *A. archangelica* showed different responses to Cu^{+} ions correlated to the light conditions [92]. The highest accumulation of cardenolides have been reported in *Digitalis purpurea* L. by obtained under Red and Blue combination or Blue alone LEDs light [88]. Alvarado-Orea *et al*. 2020 [91] reviewed that the long exposure to the white light elicitor induces the photoreceptors in the cell cultures, which in turn, lead to specific genes expression, responsible for various functions of development, and secondary metabolites synthesis. On the other hand, UV radiation, like (UV-A, UV-B and UV-C) positively applied as one of the abiotic elicitors, for enhancing various groups of secondary metabolites contents in different plant species [93,94]. In this contex, UV-B light treatment in *Catharanthus roseus* plants, hairy roots cultures and cell suspension cultures showed significant increases in the accumulation of total alkaloids as lochnericine, serpentine and ajmalicine that are precursors for vinblastine and vincristine, important bioactive compounds, for treating leukemia and lymphoma [95]. UV-C irradiation enhanced production of resveratrol's in grape genotype callus cultures [96]. The contents of flavonoids and hypericin in plantlets of *Hypericum retusum Aucher*, grown under in vitro conditions were enhanced after the exposure for 45 minutes to the UV-B radiation, comparing to their contents in the untreated growing plants [97]. Eldawayati et al. (2021) [98] enhanced total steroids accumulation in date palm callus culture by high light intensity.

Temperature. The principle key for many physiological mechanisms of the rate of intracellular reactions, nutritional needs, permeability and metabolic regulation in plant cell cultures is the temperature, therefore, any change in the culture temperature may lead to a change in the metabolism of cultured cells, which subsequently affect the growth and secondary metabolite accumulation [57]. The suitable temperature for callus induction and cell culture growth normally is ranging of 17–25 °C [99]. On the other hand, the extremely increased or decreased in temperature is considered as an adverse environmental factor restricting development and productivity of plant, it also manipulates various metabolic processes including the synthesis and degradation of primary metabolites in plant cells [93,63]. That there is a different temperature may favor for each cell culture in *Perilla frutescens* and strawberry cultures, anthocyanin yield has maximized at Optimum temperature (25 °C) [100]. Meanwhile, in *Digitalis lanata* cell cultures, the incubation temperature at 19 °C was favored for biotransformation of digitoxin to digoxin, whereas, at 32 °C, it was optimal for the formation of purpureaglycoside-A formation. In addition, in *Melastoma malabathricum* cell cultures at a low temperature range about 20 °C had higher anthocyanin production. Where in *Nicotiana tabacum* cell cultures, the ubiquinone yield was higher at 32 °C when compared to 24 °C; also, in *Melastoma malabathricum* cell cultures at a low temperature range about 20 °C had higher anthocyanin production. [56,57,93].

Salinity. Conditions are usually induced by the activity of salt ions, which involves complex physiological traits. Salt stress triggers biosynthesis for several secondary metabolites in plant cells and has a great impact for elicitation strategy for many bioactive compounds [101,102,103]. Hyperin and isoquercitrin accumulation in callus cultures of *Apocynum venetum* were successfully obtained at 150 mMol L^{-1} Sodium chloride (NaCl) in MS medium [104]. Gupta et al 2014 [105], demonstrate that salt stress by using 10 % NaCl and 0.025% Sodium carbonate (Na_2CO_3) enhanced the steviol glycosides content in suspension culture of *Stevia rebaudiana*. The highest alizarin and purpurin contents in cell suspension cultures of *Rubia tinctorum* L. at 200 mMol NaCl concentration of salt stress [106]. Golkar et al. 2019 [107] investigated the effects of different concentrations of sodium alginate on the production of secondary metabolites and antioxidant activity of seven safflower callus under in vitro salinity stress.

Heavy Metals. Elicitation by heavy metals is one of the chemical means for plant secondary metabolites production. Recently, literature announced novel compounds produced from plants and microorganisms through using the metal-stress mechanism [108]. Heavy metals are elements with a density greater than 5 g cm^{-3}, not all of them are incorporated in the field of biology. Among them, only copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn), are utilized at a trace amount metal as a micronutrient for the living plant cells, however, at high concentrations they result in toxicity. On the other hand, Silver, Mercury, Cadmium, Antimony and Lead are toxic to microorganisms [108]. Heavy metals have immense possibilities to stimulate the production and accumulation of valuable SMs in hairy root cultures as well as in plant cell cultures of different plant species. [94]. Shikonin production in *Lithospermum* callus cultures was enhanced by treating Cu^{2+} and Cd^{2+} [109]. Accumulation of cardenolide induced in *Digitalis lanata* tissue cultures by high $MnSO_4$ levels [110]. Similarly, copper ions induced the accumulation of hecogenin in *Agave amaniensis* suspension culture [111], betalains in *Portulaca* suspension culture [112], and anthocyanins in *ohelo* suspension culture. Scopoletin accumulation in cell suspension cultures of *Angelica archangelica* was effectively improved by Copper (II) sulfate elicitor [91]. In date palm cv. Sewi callus cultures, steroids production stimulated by using different concentrations of Cadmium Chloride at (0.05and 0.1 gL^{-1}) or Aluminum Chloride at (0.03 and 0.06 gL^{-1}), results showed that $CdCl^2$ at 0.1 g L^{-1} recorded the maximum value of total steroid content (0.97mg g^{-1} dw), [113]

Osmotic and Stress Chemicals Compounds. The production of secondary metabolites is greatly influenced by plant growth conditions. It is well known that, osmotic stress conditions, is usually parallel with increases in secondary metabolite production in plants, due to various changes in metabolic defense and gene expressions in plant cells. Thus, optimization of osmotic factors is critically important for large-scale production of plant secondary metabolites in bioreactors [57,114]. Higher sucrose concentrations (7 and 9 %) showed promotes effect on the metabolite production of caffeic acid derivatives of *Echinacea angustifolia* in a pilot-scale bioreactor [115]. Capsaicin accumulation in the suspension cultures of *Capsicum chinses* Jacq. cv, was significantly affected using sucrose and mannitol as osmotic conditions [114]. The influence of osmotic agents in enhancing the accumulation of taxane and paclitaxel in suspension cell cultures of *Taxus chinensis* was investigated by [116]. Mannitol sugar in conservation medium showed a reduction in total steroids contents of conserved callus of date palm [117].

Various studies employed polyethylene glycol (PEG) at high concentrations in the culture medium as osmotic stress to induce secondary metabolites production [118]. Presence of higher dose of polyethylene glycol led to different metabolic changes in plant cell culture, due to it exhibited water deficit and drought stress condition [119].

Polyethylene glycol enhanced the production of steviol glycoside in callus and suspension culture of *Stevia rebaudiana* [120]. Alzandiand Naguib 2020 [121]. investigated the synergetic effect of hydropriming and polyethylene glycol on improving the secondary metabolites accumulation in fenugreek callus cultures without occurrence of cell death. They found that hydropriming protected the growth of the cells under polyethylene glycol treatment with a high yield of secondary metabolites and high antioxidant machinery.

Biotic Elicitors

Enzymes from Microorganisms. Hydrolytic enzymes, excreted by fungi and/or plant cells, have elicitor activity on plants [122,123]. Moreover, proteins and enzymes act as biotic elicitors that increased the defense reactions in different plant cell cultures, which results in secondary metabolites production in plant cells. [124]. In cultures of *Plantanus × acerifolia* with a crude elicitor preparation from *Ceratocystis fimbriata*, stimulate the metabolic synthesis of some bioactive compounds like hydroxycoumarin phytoalexins, scopoletin and umbelliferone, where only the protein-containing fraction of the culture filtrate was involved in the cell response [125,126]. The cell walls digesting enzymes cellulose and pectolyase from *Aspergillus japonicus* are applied to enhance paclitaxel emission from Taxus canadensis cell suspension cultures. However, members of the fungal Aspergillus genus are widely used for the production of polysaccharide-degrading enzymes [127,128] Yeast extract is commonly used as a microbial elicitor, it is commercially produced by the digestion of yeast via exogenous or endogenous enzymes or in acidity conditions. It is successfully applied to the improvement of secondary metabolites synthesis in the plant cell suspension culture systems [128]. In *Linum album* yeast extract enhanced the accumulation of podophyllotoxin [129], also, rosmarinic acid in *Solenostemon scutellarioides* [130]. Gantait and Panigrahi 2018 [131] reported that biotic election using yeast inoculation, highly increased the yield of vasicine pyrroloquinazoline alkaloids in callus culture of *Adhatoda vasica* Nees.

Fungi and Bacteria Attacks. The pathogen itself and its derivatives are included among biotic elicitors. It was found that in the incipient studies on the stimulation of secondary metabolites accumulation in plant cell cultures, elicitation procedures have been accomplished, using the biological derivatives and pathogen mixtures. [132] where many secondary metabolic components induced by microbial invasion, have good results for many important bioactive compounds. Bacterial extracts, yeast extracts, and fungal extracts are biological preparations with the unknown molecular structure of the ingredients, they have an activation influence on the plant defense responses, that leads to the synthesis of secondary metabolites [62,128]. Bacterial extracts have been successfully used to enhance the accumulation of ginsenosides in P. ginseng hairy roots [133]. Kang et al. 2009 [134] found that in cell suspension culture of G. *biloba*, production of bilobalide, ginkgolide and ginkgolide, positively increased with treatment of *Candida albicans* and *Staphylococcus aureus* as biotic elicitors. In Beta vulgaris, hairy roots culture the enhancement of betalain accumulation increased by treatment of whole microbial extracts [135]. Microbial co-culture strategy is recently applied to enhance secondary metabolites production from plant cell cultures [128]. On the other hand, the effect of using endophytic bacteria of *Panax ginseng* has been studied to enhance the ginsenoside accumulation in adventitious ginseng root culture [136]. Many studies reported about the significant effects of fungal elicitation on the stimulation of plant secondary metabolites, In *Euphorbia pekinensis* cell suspension cultures, terpenoid and polyphenol accumulation were induced by using endogenous fungal elicitor [137]. The production of forskolin in cell suspension cultures of *Coleus forskohlii* increased up to 6-fold after the elicitation treatment with different fungal elicitors [138]. Elicitation with an *Aspergillus niger* extract in suspension cultures of *Andrographis paniculata*, significantly increased the flavonoid production. [139]. Fungal preparations extracts from both Aspergillus *niger* and *Penicillium notatum* fungal, improved the accumulation of psoralen in cell cultures of *Psoralea corylifolia* [140]. Simic et al 2015 [141] observed a significant increase in naphtodianthrones, total phenolic, flavonoids and anthocyanins in treated H. *perforatum* cell suspensions. Various fungal extracts, could be used separately or in combination with other elicitors, in many Taxus species, to provoke the yields of paclitaxel and other taxanes *in vitro* cultures [142]. Endophytic fungi *Chaetomium globosum* and *Paraconiothyrium brasiliense* induced paclitaxel synthesis in *Corylus avellana* cell suspension culture [143]. Taha et al. 2012 [87] clearly indicated that, the combination of both biotic elicitors of *Aspergillus niger* extract and methyl jasmonate (MJ) showed a critical role in enhancing the total phenolic and peroxides accumulation in date palm cell suspension.

Chitosan, Salicylic Acid and Methyl jasmonate. Chitin and Chitosan have been used as biotic elicitors as they are originally derivatives from a number of living organisms. [144,145]. In Cistanche deserticola cell suspension cultures, the Phenylethanoid glycoside accumulation greatly improved after using the chitosan under the optimal conditions [146]. Also, Chitosan addition activates the triterpenoid contents in the cell suspension cultures of *Betula platyphylla* Suk [147]. The separately supplemented with chitin or chitosan enhanced the paclitaxel production in cell suspensions of T. chinensis [148]. Chitosan enhanced the accumulation of hydrolysable tannin in *Phyllanthus debilis Klein* ex Willd cell suspension culture [149].

Methyl jasmonate. (MeJa) plant hormone derivative, have been well documented for its vital role in particular signal for transduction processes, that regulate the defense genes in plants, leading to the pathways of the biosynthesis of the secondary metabolites. MeJa positively stimulates the production of a diversity of plant secondary metabolites, including terpenoids, flavonoids, alkaloids, and phenylpropanoids, when applied to various plant cell cultures of different species [129,150]. The external addition of MeJa to the Taxus cell cultures has been considered one of the first in vitro cell culture systems, that gives demonstrated results for the paclitaxel bioactive compound production. [151]. Meanwhile, using MeJA elicitation in Panax ginseng Meyer cultures, improved the ginsenosides accumulation [152]. (Gantait and Panigrahi 2018) [131] reported that high results in accumulation of vasicine pyrroloquinazoline alkaloids in callus culture of *Adhatoda vasica* Nees by the biotic election of both of (MeJA) and yeast inoculation together. Taha et al 2012 [87], found that using methyl jasmonate (MeJA) elicitor, in the date palm cell suspension culture, have a critical role in stimulating the total phenolic and peroxides accumulation.

Salicylic Acid. (SA) has essential vital role in plant defense, by inducing systemic resistance to many pathogens [129] It has a wide range of application as a secondary metabolism elicitor, where a rapid SA accumulation takes place in the site of pathogens hitting, leading to signal movement to other parts of the plant to induce a broad range of defense reactions, coupled with a series of processes of secondary metabolites production in the plant cells. [89,94]. Ginsenoside production was enhanced by SA elicitation in P. ginseng adventitious roots [153]. *Withania somnifera* Adventitious roots cultures exhibited an accretion in the accumulation of the anti-inflammatory withanolides followed the SA treatment. [82]. The production of anticancer compound dicentrine in callus and cell suspension *of Stephania venosa*, positively increased by SA elicitation [154]. Stilbene synthesis was induced significantly in cell suspension cultures of V. *vinifera* by the influence of SA, separately or coupled with other elicitors treatments [155].

Conclusions and Prospects

The date palm tree is a renewable source for primary raw materials, which can be implicated beneficially in various applications in human life. It is considered as a sustainable, easily available and alternative cheap, and could inspire future researches for utilizing such renewable biomass, for generating new energy sources. On the other hand, using the in vitro technology strategy, gave higher opportunity to the production of plants biomass secondary metabolites. Cell suspension and bioreactors technology, are the promising protocols for the production of secondary metabolites of medicinal plants. There is a large amount of important bioactive compounds of date palm, can be utilized for the medicinal products, despite of the limited studies achieved in this approach.

In general, the production of the various bioactive compounds of date palm by tissue culture approach, can be achieved by optimization culture media and environment conditions, using the appropriate biosynthetic precursors feeding and using optimized elicitation strategy of biotic and abiotic stress. The pharmaceutical industry in date palm needs a proper understanding and Intensive analysis of different strategies, that would permit the way towards successful bioprocesses production of the valuable bioactive compounds.

References

[1]- C. Chao, R.R. Krueger, The date palm (*Phoenix dactylifera* L.): overview of biology, uses, and cultivation. HortScience 42(5) (2007)1077–1082 doi: doi.org/10.21273/HORTSCI. .42.5.1077

[2]- A. El Hadrami, J.M. Al-Khayri, Socioeconomic and traditional importance of date palm. Emir J food Agric 24(5) (2012) 371–385

[3]- M. Tengberg, Beginnings and early history of date palm garden cultivation in the Middle East. J Arid Environ 86(1) (2012)139–147. doi: 10.1016/j.jaridenv.2011.11.022

[4]- S. Gantait, M.M. El-Dawayati, J. Panigrahi, C. Labrooy, S. Kumar Verma, The retrospect and prospect of the applications of biotechnology in (*Phoenix dactylifera* L.), App.Microbiol. and biotech.102 (19) (2018), 8229-8259.

[5]- D. Johnson., Introduction: date palm biotechnology from theory to practice. In: Jain SM, [6]-Al-Khayri JM, Johnson D (eds) Date palm biotechnology. Springer, Dordrecht (2011) pp 1–11. doi: 10.1007/978-94-007-1318-5

[7]- S. Jain M., Date palm biotechnology: Current status and prospective-an overview. Emirates J food Agric 24 (5) (2012)386–399

[8]- R. Al-Alawi, J.H. Al-Mashiqri, J.S.M. Al-Nadabi, et al, Date palm tree (*Phoenix dactylifera* L.)- Natural products and therapeutic options. Front. Plant Sci. 8 (845) (2017) 1–12. doi: 10.3389/fpls.2017.00845

[9]- A. Zaid, P.F. de Wet, Botanical and systematic description of the date palm. In: Zaid A (ed), Date palm cultivation. Rome, Italy: FAO, Plant Production and Protection (2002) pp. 1–25

[10]- M.A. Afiq, R.A. Rahman, Y.C. Man, H.A. Al-Kahtani, T.S.T Mansor, Date seed and date seed oil. Int. Food Res. J., 20(5) (2013) p.2035.

[11]- Z.X. Tang, L.E. Shi, S.M. Aleid, Date fruit: chemical composition, nutritional and medicinal values, products. J Sci Food Agric 93(10) (2013) 2351–2361.

[12]- S. Ghnimi, R. Almansoori, Quality evaluation of coffee-like beverage from date seeds *Phoenix dactylifera* L, J. Food Proc. Tech. 6 (2015)1–6

[13]- R. Salomón-Torres, B. Valdez-Salas, S. Norzagaray-Plasencia, Date Palm: Source of Foods, Sweets and Beverages. In The Date Palm Genome*,* 2, 2021 pp. 3-26. Springer, Cham.

[14]- M., Chandrasekaran, A.H. Bahkali, Valorization of date palm (*Phoenix dactylifera* L.) fruit processing by-products and wastes using bioprocess technology–Review. Saudi J. Biol. Sci. 20(2) (2013) 105–120.

[15]- M.Q. Al-Mssallem, R.M. Alqurashi, J.M. Al-Khayri, Bioactive compounds of date palm (*Phoenix dactylifera* L.). In: H. N. Murthy, V. A. Bapat (eds.), Bioactive Compounds in Underutilized Fruits and Nuts, Reference Series in Photochemistry. 2019 pp 1–11. Springer Nature, Switzerland, doi.org/10.1007/978-3-030-06120-3_6-1

[16]- R.A. Nasser, M.Z.M. Salem, S. Hiziroglu et al, Chemical analysis of different parts of date palm (*Phoenix dactylifera* L.) using ultimate, proximate and thermo-gravimetric techniques for energy production. Energies 9 (2016) 374. Doi: 10.3390/en9050374

[17]- W., Ghori, N., Saba, M., Jawaid, M., Asim, A review on date palm (*phoenix dactylifera*) fibers and its polymer composites. In (IOP conference series: materials science and engineering, 368(1) 2018 p. 012009). IOP Publishing.

[18]- S. Awad, Y. Zhou, E. Katsou, et al. A Critical Review on Date Palm Tree (*Phoenix dactylifera* L.) Fibres and Their Uses in Bio-composites. Waste Biomass (12) 2021, 2853–2887.

[19]- G. Kabir, B.H Hameed, Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals. Renewable and Sustainable Energy Reviews, Materials Sci. Forum Vol. 1051 (70) (2017) 945-967.

[20]- Y. Makkawi, Y. El Sayed, M. Salih, P. Nancarrow, S. Banks, T. Bridgwater, Fast pyrolysis of date palm (*Phoenix dactylifera*) waste in a bubbling fluidized bed reactor. Renewable energy (143) (2019) 719-730.

[21]- R.A. Nasser, H.A. Al-Mefarrej, Midribs of date palm as a raw material for wood-cement composite industry in Saudi Arabia. World Appl. Sci.J. 15(12) (2011) 1651–1658.

[22]- A.R.A. Usman, A. Abduljabbar, M. Vithanage et al, Biochar production from date palm waste: Charring temperature induced changes in composition and surface chemistry. J. Anal. Appl. Pyrolysis (115) (2015) 392–400 doi.org/10.1016/j.jaap.2015.08.016

[23]- M.A. Al-Farsi, C.Y. Lee, Nutritional and functional properties of dates: A review. Crit. Rev. Food Sci. Nutr. 48(10) (2008) 877–887. doi: 10.1080/10408390701724264

[24]- M. Ramchoun, C. Alem, K. Ghafoor, J. Ennassir, Y. F .Zegzouti, Functional composition and antioxidant activities of eight Moroccan date fruit varieties (*Phoenix dactylifera L.*). J. Saudi Soci.Agr. Sci, 16(3) (2017) 257-264.

[25]- A.M. Martín-Sánchez, S. Cherif, J. Ben-Abda, X. Barber-Vallés, J.Á. PérezÁlvarez, [25]-E., Sayas-Barberá, Phytochemicals in date co-products and their antioxidant activity. Food Chem. (158) (2014) 513–520.

[26]- F. Biglari, A.F. Al Karkhi, M. Easa, Antioxidant activity and Phenolic content of various date palm (*Phoenix dactylifera* L.) fruits from Iran. Food Chem. 107(2007) 1636–1641.

[27]- A. El Hadrami, F. Daayf, I. El Hadrami Secondary metabolites of date palm. In: Jain S, Al-Khayri J, Johnson D (eds) Date palm biotechnology. Springer, Dordrecht pp 653–674 doi:10.1007/978-94-007-1318-5

[28]-Daayf F, Lattanzio V (2009) Recent advances in polyphenol research, Wiley Inter Science, New York. Vol 1

[29]- P.M. Naik, J.M. Al-Khayri, Cell suspension culture as a means to produce polyphenols from date palm (*Phoenix dactylifera* L.). Ciência e Agrotecnologia 42(5) (2018):464–473

[30]- L.U. Thompson, B.A. Boucher, Z. Liu, et al, Phytoestrogen content of foods consumed in Canada, including isoflavones, lignans, and coumestan. Nutr. Cancer 54(2006)184–20

[31]- E.A. Amira, S.E. Behija, M. Beligh, L. Lamia, I. Manel, H. Mohamed, et al, Effects of the ripening stage on phenolic profile, phytochemical composition and antioxidant activity of date palm fruit. J. Agric. Food Chem. 60(2012) 10896–10902. doi: 10.1021/jf302602v

[32]- M. Lemine, F. Mint, M.V.O., Mohamed Ahmed, L. Ben Mohamed Maoulainine, Z. Bouna et al. Antioxidant activity of various Mauritanian date palm (*Phoenix dactylifera* L.) fruits at two edible ripening stages. Food Sci. Nutr. 2(2014) 700–705. doi: 10.1002/fsn3.167

[33]- Y.J. Hong, F.A. Tomas-Barberan, A.A, Kader, A.E. Mitchell, The flavonoid glycosides and procyanidin composition of deglet noor dates (*Phoenix dactylifera*). J. Agric. Food Chem. 54(2006) 2405–2411doi: 10.1021/jf0581776

[34]- I. Hamad, H., Abd Elgawad, S., Al Jaouni et al Metabolic analysis of various date palm fruit (*Phoenix dactylifera* L.) cultivars from Saudi Arabia to assess their nutritional quality. Molecules 20(8) (2015) 13620–13641

[35]- H. Borochov-Neori, S., Judeinstein, A., Greenberg, N. Volkova, M. Rosenblat, M. Aviram Antioxidant and antiatherogenic properties of phenolic acid and flavonol fractions of fruits of Amari and Hallawi date (Phoenix dactylifera L.) varieties. J. Agric. Food Chem. 63(2015) 3189–3195. doi: 10.1021/jf506094r

[36]- M., Al-Farsi, C, Alasalvar, A., Morris, et al. Comparison of antioxidant activity, anthocyanins, carotenoids, and phenolics of three native fresh and sun-dried date (*Phoenix dactylifera* L.) varieties grown in Oman. J Agric Food Chem 53(2005)7592–7599 53:7592–7599. doi: 10.1021/jf050579q

[37]- EB. Saafi, A., El Arem, M. Issaoui, et al, Phenolic content and antioxidant activity of four date palm (*Phoenix dactylifera* L.) fruit varieties grown in Tunisia. Int. J. food Sci. Technol. 44(11) (2009)2314–2319

[38]- N, Eid, S, Enani, G, Walton, et al, The impact of date palm fruits and their component polyphenols, on gut microbial ecology, bacterial metabolites and colon cancer cell proliferation. J Nutr Sci 3: (2014). e46 doi: 10.1017/jns

[39]- D.J. Thanekar, N. Dhodi, Gawali et al, Evaluation of antitumor and anti-angiogenic activity of bioactive compounds fromCinnamomum tamala: In vitro, in vivo and in silico approach South African J. Bot. 104(2016) 6–14.

[40]- H. El Abed, M. Chakroun, Z. Abdelkafi-Koubaa, N. Drira, N. Marrakchi, H. Mejdoub, [41]-B. Khemakhem. Antioxidant, anti-inflammatory, and antitumoral effects of aqueous ethanoic extract from Phoenix dactylifera L. parthenocarpic dates. BioMed Res. Int.(2018) https://doi.org/10.1155/2018/1542602

[42]- R.R. Pujari, N.S. Vyawahare, V.G. Kagathara, Evaluation of antioxidant and neuroprotective effect of date palm (Phoenix dactylifera L.) against bilateral common carotid artery occlusion in rats Indian J. Exp. Biol 49(8) (2011) 627–633.

[43]- M.D. Garba, A. Galadima. Anti-diarrhoea and phytochemical evaluation of (Phoniex dactylifera L.) extracts. Elixir Appl. Chem 49(2012) 9808–9812

[44]- S. Belmir, K. Boucherit, Z., Boucherit-Otmani, M.H. Belhachemi, Effect of aqueous extract of date palm fruit (*Phoenix dactylifera* L.) on therapeutic index of amphotericin B. Phytothérapie 14(2016)97–101

[45]- S.F. El-Sharabasy. Studies on the production of secondary metabolites from date palm by using tissue culture technique. Ph.D. Thesis, Fac Agric, Al-Azhar University, Cairo (2000) pp 200.

[46]- A.H.S. Rahman, M. Aly, H. Ali, et al, Therapeutic effects of date fruits (*Phoenix dactylifera*) in the prevention of diseases via modulation of anti-inflammatory, anti-oxidant and antitumour activity, Int. J. Clin. Exp.Medc.7(2014) 3483–491.

[47]- N. Zangiabadi, M. Asadi-Shekaari, V. Sheibani, et al, Date fruit extract is a neuroprotective agent in diabetic peripheral neuropathy in streptozotocin-induced diabetic rats: a multimodal analysis. Oxid Med Cell Longev, 2011 pp 9. doi: 10.1155/2011/976948.

[48]- G. Guerrier, R., Berni, J.A. Muñoz-Sanchez, et al. Production of plant secondary metabolites: Examples, tips and suggestions for biotechnologists. Genes (Basel) 9(6) (2018) pp 309.

[49]- R.A. Hussein, A.A. El-Anssary, Plants secondary metabolites: the key drivers of the pharmacological actions of medicinal plants. In Herbal Medicine. Intech Open (2018)

[50]- M. Mazid, T.A. Khan, F. Mohammad. Role of secondary metabolites in defense mechanisms of plants. Biol Med 3(2) (2011)232–249

[51]- S.S. ul Hassan, H. Jin, T. Abu-Izneid, et al. Stress-driven discovery in the natural products: A gateway towards new drugs. Biomed Pharmacother 109(2019) 459–467.

[52]- S.A. Wilson, S.C. Roberts. Recent advances towards development and commercialization of plant cell culture processes for the synthesis of biomolecules. Plant Biotechnol J 10(3) (2012)249–268

[53]- A.G. Atanasov, B. Waltenberger, E.M. Pferschy-Wenzig, et al, Discovery and resupply of pharmacologically active plant-derived natural products: A review. Biotechnol Adv 33(8) (2015)1582–1614

[54]- S.N., Jimenez-Garcia, M.A., Vazquez-Cruz, R.G., Guevara-Gonzalez, et al. Current approaches for enhanced expression of secondary metabolites as bioactive compounds in plants for agronomic and human health purposes–a review. Polish J Food Nutr Sci 63(2) (2013) 67–78.

[55]- P. Ahmad, M.A. Ahanger, V.P. Singh, et al, Plant metabolites and regulation under environmental stress. Academic Press 1st Edition. (2018) e Book ISBN: 9780128126905

[56]- S. Manorma, S. Archana, K. Ashwani, et al, Enhancement of secondary metabolites in cultured plant cells through stress stimulus. Am J Plant Physiol 6(2) (2011) 50–71.

[57]- M. Narayani, S. Srivastava. Elicitation: a stimulation of stress in in vitro plant cell/tissue cultures for enhancement of secondary metabolite production. Phytochem Rev 16(6) (2017)1227–1252

[58]- I., Smetanska. Production of secondary metabolites using plant cell cultures. In: Food biotech.. Springer, Berlin, Heidelberg(2008) pp 187–228

[59]- P.M., Naik, J.M., Al-Khayri. Impact of abiotic elicitors on in vitro production of plant secondary metabolites: a review. J Adv Res Biotech 1(2) (2016)7. doi: http://dx.doi.org/10.15226/2475-4714/1/2/00102

[60]- M. Ochoa-Villarreal, S. Howat, S. Hong, et al, Plant cell culture strategies for the production of natural products. BMB Rep 49(3) (2016) 149

[61]-Kreis W (2019) Exploiting plant cell culture for natural product formation. J Appl Bot FOOD Qual 92:216–225.

[62]- J.C. Cardoso, M.E. Oliveira, F. Cardoso, Advances and challenges on the in vitro production of secondary metabolites from medicinal plants. Hortic Bras 37(2) (2019)124–132.

[63]- N. Khanpour-Ardestani, M., Sharifi, M., Behmanesh. Establishment of callus and cell suspension culture of *Scrophularia striata* Boiss.: an in vitro approach for acteoside production. Cytotechnology 67(3) (2015)475–485.

[64]- S.F. El Sharabasy. Effect of some Micro-Elements on Steroids Production from Embryogenic Callus of in vitro Date Palm Sakkoty and Bartamuda Cultivars. Materials Research Proceedings, 11. (2019).

[65]- T. Isah, Stress and defense responses in plant secondary metabolites production. Biol. Res. 52(1) (2019) 39

[66]- C.A. Espinosa-Leal, C.A. Puente-Garza, S. Garcia-Lara. In vitro plant tissue culture: means for production of biological active compounds. Planta 248(1) (2018)1–18.

[67]- A.N. Shinde, N. Malpathak, D.P. Fulzele. Studied enhancement strategies for phytoestrogens production in shake flasks by suspension culture of *Psoralea corylifolia*. Bioresour. Technol. 100(5) (2009)1833–1839.

[68]- S.Z.M.R., Jamil, E.R., Rohani, S.N., Baharum, N.M., Noor. Metabolite profiles of callus and cell suspension cultures of *mangosteen.* 3 Biotech 8(8) (2018) p322

[69]- P.M. Naik, J.M., Al-Khayri. Extraction and estimation of secondary metabolites from date palm cell suspension cultures. In Date Palm Biotechnology Protocols Volume, Humana Press, New York, NY I (2017) pp. 319–332

[70]- K. Gokulan, S., Khare, C., Cerniglia. Metabolic Pathways: Production of secondary metabolites of bacteria. In: Batt CA, Tortorello ML (eds.), Encyclopedia of Food Microbiology, vol 2. Elsevier Ltd, Academic Press (2014) pp 561–569

[71]- F.R. Pinu, S.G. Villas-Boas, R., Aggio. Analysis of intracellular metabolites from microorganisms: quenching and extraction protocols. Metabolites 7(4) (2017) 53.

[72]- B. Andryukov, V. Mikhailov, N. Besednova, The biotechnological potential of secondary metabolites from marine bacteria. J Mar Sci Eng 7(6) (2019)176.

[73]- M. Behbahani, M. Shanehsazzadeh, M.J. Hessami, Optimization of callus and cell suspension cultures of *Barringtonia racemosa* (Lecythidaceae family) for lycopene production. SCI AGR 68(1) (2011) 69–76

[74]- S.F., El-Sharabasy. Effects of some precursors on development of secondary products in tissues and media of embryogenic callus of date palm cv. Sewi Arab. J Biotechnol 7(1) (2004)83–90.

[75]- H.S. Taha, A.M., Abdel-El Kawy, M.A.E.K. Fathalla, et al. Implement of DMSO for enhancement and production of phenolic and peroxides compounds in suspension cultures of Egyptian date palm (Zaghlool and Samany) cultivars. J Biotech Biochem 1(2010) pp 1–10.

[76]- M. Jalil, M.S.M. Annuar, B.C. Tan, et al, Effects of selected physicochemical parameters on zerumbone production of *Zingiber zerumbet* Smith cell suspension culture. Evid Based Complement Alternat Med (2015) 7 pages, Article ID 757514 doi.org/10.1155/2015/757514

[77]- Q. Li, M. Tang, Y. Tan, et al. Improved production of chlorogenic acid from cell suspension cultures of *Lonicera macranthoids*. Trop J Pharm Res 15(5) (2016) 919-927

[78]- A. Valdiani, O.K. Hansen, U.B. Nielsen, et al, Bioreactor-based advances in plant tissue and cell culture: challenges and prospects. Crit Rev Biotechnol 39(1) (2019) 20–34

[79]- M.I. Georgiev, R. Eibl, J.J. Zhong, Hosting the plant cells in vitro: recent trends in bioreactors. Appl Microbiol Biotechnol 97(9) (2013)3787–3800.

[80]- S. Werner, R.W. Maschke, D. Eibl, R. Eibl, Bioreactor technology for sustainable production of plant cell-derived products. Bioprocessing of Plant In Vitro Systems 2018 pp 413–432.

[81]- R. Eibl, D. Eibl, Plant cell-based bioprocessing. In Cell and Tissue Reaction Engineering Springer, Berlin, Heidelberg 2009 pp. 315–356.

[82]- G. Sivanandhan, M. Arun, S. Mayavan, et al, Optimization of elicitation conditions with methyl jasmonate and salicylic acid to improve the productivity of with an olides in the adventitious root culture of *Withania somnifera* (L.) Dunal. Appl. Biochem. Biotechnol 168(3) (2012) 681–696.

[83]- Y. Yang, M. Sha. A. Beginner's, Guide to Bioprocess Modes–Batch, Fed-Batch, and Continuous Fermentatio.n Eppendorf. Application Note (2019) (408).

[84]- L. Palacio, J.J. Cantero, R. Cusido, et al, Phenolic compound production by *Larrea divaricata* Cav. plant cell cultures and effect of precursor feeding. Process, Biochem 46(1) (2011) 418–422.

[85]- S. El-Sharabasy, M. El-Dawayati, Bioreactor steroid production and analysis of date palm embryogenic callus. In Date Palm Biotechnology Protocols, Humana Press, New York, NY Volume I 2017 pp 309–318.

[86]- Y-T. Chen, Y-C. Shen, M-C. Chang, et al, Precursor-feeding strategy on the triterpenoid production and anti-inflammatory activity of *Antrodia cinnamomea*. Process Biochem 51(8) (2016) 941–949.

[87]- H.S. Taha, S.A. Bekheet, M.K. El-Bahr, A new concept for production and scaling up of bioactive compounds from Egyptian date palm (Zaghlool) cultivar using bioreactor. Emir J Food Agr. (2012) pp 425–433.

[88]- S.K. Verma, S. Gantait, B.R. Jeong, S.J. Hwang, Enhanced growth and cardenolides production in *Digitalis purpurea* under the influence of different LED exposures in the plant factory. Sci Rep 8(1) (2018)1–12.

[89]- U. Tariq, M. Ali, B.H. Abbasi, Morph-genic and biochemical variations under different spectral lights in callus cultures of *Artemisia absinthian* L. J. Photochem. Photobiol. B: Biology 130 (2014) 264-271.

[90]- S.A. Ahmed, M. Baig, MV, Biotic elicitor enhanced production of psoralen in suspension cultures of *Psoralea corylifolia* L. Saudi J Biol Sci 21(5) (2014) 499–504.

[91]- D. Alvarado-Orea, J Paniagua-Vega, Capataz-Tafur, et al, Photoperiod and elicitors increase steviol glycosides, phenolic, and flavonoid contents in root cultures of Stevia rebaudiana. In Vitro Cell.Dev.Biol.-Plant 56(2020) 298–306 doi.org/10.1007/s11627-019-10041-3

[92]- T. Siatka, J. Chlebekb, A. Hoštálkov, Copper (II) sulfate stimulates scopoletin production in cell suspension cultures of Angelica archangelica. Nat Prod Common. 12(11) (2017)1779–1780.

[93]- R Akula, GA Ravishankar, Influence of abiotic stress signals on secondary metabolites in plants. Plant Signal Behav 6 (11) (2011) 1720–1731.

[94]- M. Halder, S. Sarkar, S. Jha, (2019) Elicitation: A biotechnological tool for enhanced production of secondary metabolites in hairy root cultures. Eng Life Sci 19(12):880–895

[95] B.Y. -Binder, C.A. Peebles, J.V. Shanks, K.Y. San, The effects of UV-B stress on the production of terpenoid indole alkaloids in *Catharanthus roseus* hairy roots. Biotechnol. Prog 25(3) (2009) 861–865.

[96]- W. Liu, C. Liu, C. Yang, et al, Effect of grape genotype and tissue type on callus growth and production of resveratrols and their piceids after UV-C irradiation. Food Chem 122(3) (2010) 475–481.

[97]- S. Namlı, Ç. Işıkalan, F. Akbaş, Toker Z, E.A. Tilkat, Effects of UV-B radiation on total phenolic, flavonoid and hypericin contents in *Hypericum retusum Aucher* grown under in vitro conditions. Nat Prod Res 28(24) (2014) 2286-2292.

[98]- M.M. El-Dawayati, S. El-Sharabasy, S. Gantait, Light Intensity-Induced Morphogenetic Response and Enhanced β-Sitosterol Accumulation in Date Palm *Phoenix dactylifera* L. cv. Hayani) Callus Culture. Sugar Tech (22) (2020) 1122-1129.

[99] Y. Xu, H. Du, B. Huang, Identification of metabolites associated with superior heat tolerance in thermal bent grass through metabolic profiling. Crop Sci., 53(4) (2013) 1626–1635.

[100]- A. Ramakrishna, G.A. Ravi Shankar, Influence of abiotic stress signals on secondary metabolites in plants. Plant Signal Behav, 6 (2011) 1720–1731.

[101]- B. Gupta, B., Huang Mechanism of salinity tolerance in plants: physiological, biochemical, and molecular characterization. Int. J Genomics, (2014) 1–18.

[102]- M. Al Hassan, A. Pacurar, M.P. Lopez-Gresa, M.P. Donat-Torres, J.V. Llinares, M. Boscaiu, O Vicente (2016) Effects of salt stress on three ecologically distinct Plantago species. Plos One 11(8): doi: 10.1371/journal.pone.0160236

[103]-Iyiola Oluwakemi Oi, Y. Chutha Takahashi, S. Sunisa Enhancing secondary metabolites (emphasis on phenolic and antioxidants) in plants through elicitation and metabolomics Pak. J. Nutr 17, (2019) 4011–420.

[104]- F. Wang, Q.L. Ji, Q. Deng, Y.W. Li Effects of different culture conditions on hyperin and isoquercitrin accumulation in callus of *Apocynum venetum* L. Chinese Traditional Patent Med (2012) 10-16.

[105]- P. Gupta, S. Sharma, S. Saxena, Effect of salts (NaCl and Na_2CO_3) on callus and suspension culture of *Stevia rebaudiana* for steviol glycoside (natural sweetener) production. Appl Biochem Biotechnol, part A: enzyme engineering and biotechnology 172(6) (2014) 2894–2906.

[106]- P. Nartop, Ş. Akay, A. Gürel, Effects of Salt Stress and Inoculation Ratios in Cell Cultures of Rubia tinctorum L. SAUJS 21(3) (2017) 328–334.

[107]- P. Golkar, M. Taghizadeh, A. Noormohammadi, Effects of sodium alginate elicitation on secondary metabolites and antioxidant activity of safflower genotypes under in vitro salinity stress. In Vitro Cell Dev Biol Plant, 55(5) (2019) 527–538.

[108]- S.S. ul Hassan, H. Jin, T. Abu-Izneid, et al, Stress-driven discovery in the natural products: A gateway towards new drugs. Biomed Pharmacother 109(2019)459–467.

[109]- H. Mizukami, M. Konoshima, M. Tabata Effect of nutritional factors on shikonin derivative formation in *Lithospermum* callus cultures. Phytochemistry 16(1977):1183–1186.

[110]- Ohlsson AB, Berglund T. (1989) Effect of high $MnSO_4$ levels on cardenolide accumulation by Digitalis lanata tissue cultures in light and darkness. J Plant Physiol 135(4):505–507

[111]- S. Kartosentono, G. Indrayanto, N.C. Zaini, The uptake of copper ions by cell suspension cultures of *Agave amaniensis*, and its effect on the growth, amino acids and hecogenin content. PCTOC 68(3) (2002)287–292.

[112]- M.N.H. Bhuiyan, T. Adachi, Stimulation of betacyanin synthesis through exogenous methyljasmonate and other elicitors in suspension-cultured cells of *Portulaca*. J. Plant Physiol 160(2003) 1117–1124.

[113]- Z.E. Zayed, M.M. El Dawayati, S.F. El Sharabasy Total steroids production from date palm callus under heavy metals stress. Biosci Res 16(2) (2019) 1448–1457.

[114]- M. Kehie, S. Kumaria, P. Tandon (2014) Osmotic stress induced-capsaicin production in suspension cultures of *Capsicum chinense* Jacq.cv. Naga King Chili. Bioprocess Biosyst Eng 37(6):1055–63

[115]- H.Y. Cui, M.A. Baque, E.J. Lee, et al, Scale-up of adventitious root cultures of *Echinacea angustifolia* in a pilot-scale bioreactor for the production of biomass and caffeic acid derivatives. Plant Biotechnol Rep 7(3) (2013) 297–308.

[116]- Y. Dong, W. Duan, H. He, P. Su, et al, Enhancing taxane biosynthesis in cell suspension culture of *Taxus chinensis* by overexpressing the neutral/alkaline inverses gene. Process Biochem 50(4) (2015) 651–660.

[117]- M.M. El-Dawayati, Z.E. Zayed, S.F. Elsharabasy Effect of conservation on steroids contents of callus explants of date palm cv. sakkoti. Aust J Basic Appl Sci 6(5) (2012) 305–310.

[118]- M. S. Bhattacharya, P.K. Khosla, Puri S., Improving production of plant secondary metabolites through biotic and abiotic elicitation. J Appl Res Med Aromat Plants 12(2019)1–12.

[119]- G. Pratibha, S. Satyawati, S. Sanjay S, Biomass yield and steviol glycoside production in callus and suspension culture of *Stevia rebaudiana* treated with proline and polyethylene glycol. Appl Biochem Biotechnol 176(3) (2015)863–874.

[120]- A.A. Alzandrin, D.M. Naguib, Effect of hydropriming on *Trigonella foenum* callus growth, biochemical traits and phytochemical components under PEG treatment. Plant Cell Tiss Organ Cult 141(2020) 179–190. https://doi.org/10.1007/s11240-020-01778-6

[121]- F.G. Malinovsky, J.U. Fangel, W.G. Willats, The role of the cell walls in plant immunity. Front Plant Sci 5(2014) 178.

122]- B.A. Cárdenas-Sandoval, L. Bravo-Luna, K. Bermúdez-Torres, et al, Enhancement of phenylethanoid glycosides biosynthesis in *castilleja tenuiflora* Benth. Shoot cultures with cell wall oligosaccharides from *Fusarium oxysporum* f. sp. lycopersici RACE 3. Rev Mex Ing Quim 14(3) (2015) 631–639.

[123]- Z. Angelova, S. Georgiev, W. Roos, Elicitation of plants. Biotechnol. Biotechnol. Equip. 20(2) (2006) 72–83.

[124]- I. Alami, S. Mari, A, Clérivet, A glycoprotein from *Ceratocystis fimbriata* f. sp. *platani triggers phytoalexin* synthesis in *Platanus* × *acerifolia* cell-suspension cultures. Photochemistry 48(5) (1998) 771–776.

[125]- M. Thakur, S. Bhattacharya, P.K. Khosla, S. Puri Improving production of plant secondary metabolites through biotic and abiotic elicitation. J Appl Res Med Aromat Plants 12(2019)1–12.

[126]- S.K. Anisa, S. Ashwini, K. Girish, Isolation and screening of *Aspergillus* spp. for pectinolytic activity. eJBio 9(2) (2013) 37–41.

[127]- S. Satapathy, P.M. Behera, D.K. Tanty et al, Isolation and molecular identification of pectinase producing Aspergillus species from different soil samples of Bhubaneswar regions. Bio Rxiv (2019) pp 837112. doi: doi.org/10.1101/837112

[128]- K. Ramirez-Estrada, H. Vidal-Limon, D. Hidalgo, et al, Elicitation, an effective strategy for the biotechnological production of bioactive high-added value compounds in plant cell factories. Molecules 21(2) (2016) pp182.

[129]- M. Shams-Ardakani, S. Hemmati, A. Mohagheghzadeh, Effect of elicitors on the enhancement of podophyllotoxin biosynthesis in suspension cultures of *Linum album*. Daru J. Pharm. Sci. 13(2) (2005) 56–60.

[130]- R. Sahu, M. Gangopadhyay, S. Dewanjee, Elicitor-induced rosmarinic acid accumulation and secondary metabolism enzyme activities in *Solenostemon scutellarioides*. Acta Physiol Plant 35(5) (2013) 1473–1481.

[131]- S. Gantait, J. Panigrahi, In vitro biotechnological advancements in Malabar nut (*Adhatoda vasica Nees*): Achievements, status and prospects. J Genet Eng Biotechnol 16(2) (2018)545–552.

[132]- A.G. Namdeo Plant cell elicitation for production of secondary metabolites: a review. Pharmacogn Rev. 1(1) (2007)69-79.

[133]- G.T. Jeong, D.H. Park, H.W. Ryu, et al, Production of antioxidant compounds by culture of *Panax ginseng* CA Meyer hairy roots. In: Davison B.H., Evans B.R., Finkelstein M., McMillan J.D. (eds) Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals. ABAB Symposium. Humana Press,2005 pp 1147–1157.

[134]- S.M. Kang, J.Y. Min, Y.D. Kim, et al, Effect of biotic elicitors on the accumulation of bilobalide and ginkgolides in *Ginkgo biloba* cell cultures. J. Biotechnol 139(1) (2009) 84–88

[135]- G. Savita, R. Thimmaraju, N. Bhagyalakshmi, et al Different biotic and abiotic elicitors influence beta lain production in hairy root cultures of *Beta vulgaris* in shake-flask and bioreactor. Process Biochem 41(1) (2006) 50–60.

[136]- X. Song, H. Wu, Z. Yin, et al, Endophytic bacteria isolated from *Panax ginseng* improves ginsenoside accumulation in adventitious ginseng root culture. Molecules 22(6) (2017) 837.

[137]- F.K. Gao, Y.H. Yong, C.C. Dai Effects of endophytic fungal elicitor on two kinds of terpenoids production and physiological indexes in *Euphorbia pekinensis* suspension cells. J Med Plants Res 5(18) (2011) 4418–4425.

[138]- G. Swaroopa, M. Anuradha, T. Pullaiah, Elicitation of forskolin in suspension cultures of *Coleus forskohlii* (willd.) Briq. Using elicitors of fungal origin. Current Trends in Biotechnology and Pharmacy 7(3) (2013)755–762.

[139]- V.D. Mendhulkar, M.M.A., Vakil, Chitosan and *Aspergillus niger* mediated elicitation of total flavonoids in suspension culture of *Andrographis paniculata* (Burm. f.) Nees. Sci. Bio. Pharma. J. Int. 4(4) (2013)731–740.

[140]- S.A. Ahmed, M.V. Baig, Biotic elicitor enhanced production of psoralen in suspension cultures of *Psoralea corylifolia* L. Saudi J. Biol. Sci. 21(5) (2014) 499–504.

[141]- S.G. Simic, O. Tusevski, S. Maur, et al, Fungal elicitor-mediated enhancement in phenylpropanoid and naphtodianthrone contents of *Hypericum perforatum* L. cell cultures. PCTOC 122(1) (2015)213–226.

[142]- H.N. Badi, V. Abdoosi, N. Farzin. New approach to improve taxol biosynthetic. T.J.S. 2(2015)115–124.

[143]- M. Salehi, A. Moieni, Safaie N, et al Elicitors derived from endophytic fungi *Chaetomium globosum* and *Paraconiothyrium brasiliense* enhance paclitaxel production in Corylus avellana cell suspension culture. PCTOC 136(1) (2019) 161–171.

[144]- M.M.A. Elsoud, E.M. El Kady Current trends in fungal biosynthesis of chitin and chitosan. Bull Natl Res Cent 43(1) (2019)1–12.

[145] J.I. Kadokawa, R. Shimohigoshi, K. Yamashita, et al, Synthesis of chitin and chitosan stereoisomers by thermostable α-glycan phosphorylase-catalyzed enzymatic polymerization of α-D-glucosamine 1-phosphate. Org Biomol Chem 13(14) (2015) 4336–4343.

[146]-Cheng X.Y., Zhou HY, Cui X, et al, Improvement of phenylethanoid glycosides biosynthesis in *Cistanche deserticola* cell suspension cultures by chitosan elicitor. J. Biotechnology 121(2) (2006) 253–260.

[147]-Fan G, Li X, Wang X, et al, Chitosan activates defense responses and triterpenoid production in cell suspension cultures of *Betula platyphylla* Suk. Afr. J. Biotech. 9 (19) (2010) 2816.

[148]- S.T. Li, P. Zhang, M. Zhang, et al, Transcriptional profile of *Taxus chinensis* cells in response to methyl jasmonate. BMC genomics 13(1) (2012) 295.

[149]- V. Malayaman, N. Sisubalan, R.P. Senthilkumar, et al, Chitosan mediated enhancement of hydrolysable tannin in *Phyllanthus debilis* Klein ex Willd via plant cell suspension culture. Int. J Biol. Macromol 104(2017) 1656–1663.

[150]- E. Sadeghnezhad, M. Sharifi, H. Zare-Maivan, et al, Time-dependent behavior of phenylpropanoid pathway in response to methyl jasmonate in *Scrophularia striata* cell cultures. Plant Cell Rep. (2019) 1–17.

[151]- M. Onrubia, R.M. Cusidó, K. Ramirez, et al, Bioprocessing of plant in vitro systems for the mass production of pharmaceutically important metabolites: Paclitaxel and its derivatives. Cur. Med. Chem. 20(7) (2013) 880–891.

[152]- J.Y. Oh, Y.J. Kim, M.G. Jang, et al, Investigation of ginsenosides in different tissues after elicitor treatment in *Panax ginseng*. J Ginseng Res 38(4) (2014) 270–277.

[153]- R.K. Tewari, Paek K.Y., Salicylic acid-induced nitric oxide and ROS generation stimulate ginsenoside accumulation in *Panax ginseng* roots. J. Plant Growth Regul 30(4) (2011) 396–404.

[154]- T. Kitisripanya, J., Komaikul, N., Tawinkan, et al. Dicentrine production in callus and cell suspension cultures of *Stephania venosa*. Nat. Prod. Common 8(4) (2013) 443–445.

[155]- A. Xu, J.C., Zhan, W.D., Huang Effects of ultraviolet C, methyl jasmonate and salicylic acid, alone or in combination, on stilbene biosynthesis in cell suspension cultures of *Vitis vinifera* L. cv, Cabernet Sauvignon. PCTOC 122(1) (2015) 197–211.

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Single Fiber Test Behavior of Lignocellulose Sugar Palm Fibers: Effect of Treatments

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Abstract: This paper evaluates the influence of two types of treatments on the tensile related properties of sugar palm fiber (SPF) by using a single fiber test. Natural fibers are one of the vital reinforcing materials in polymer composites due to their positive properties. Sugar palm fiber is a kind of lignocellulose fiber that can be a good potential filler material in fibers/polymer composites for many uses. A Scanning electronic microscope was used to evaluate morphological analyses. Seawater and alkaline solution treatments were used to treat the fiber before the test. The properties of sugar palm fibers improved significantly, as the effect of alkaline concentration by 0.5% and 0.25% improved the tensile properties of a single fiber by 10% and 176%, respectively compared to the untreated fiber. On the other hand, the highest effect on sugar palm fibers was the fibers treated by seawater for 30 days by 273%. Morphologic analyses showed that the treatment plays a big role to clean the surface of the fibers and remove the undesirable impurities. Overall, the results depict that the treatments improve the tensile properties of the single SPF.

Introduction

Natural fibers are deemed alternative structures that hold up or serve as a foundation in polymer matrix composites. Natural fibers have received much attention in the last years, due to their various competitive advantages over synthetic fibers, such as biodegradability, weight reduction, low cost, and availability [1]. Sugar palm fiber (SPF) is a natural-derived fiber that is widely considered to be important for many researchers in the bio-composite materials field. It is obtained from four different parts of the sugar palm tree (Arenga Pinnata palm tree); namely trunk, bunch, frond, and the trunk surface (Ijuk) [2].

In recent years, there has been growing interest in replacing synthetic fibers with naturally derived ones to reinforce bio-composites [3, 4]. Fibers including jute, kenaf, hemp, flax, and roselle have been indicated as being to have improved polymer composites reinforcing abilities [5]. Some types of natural fibers have been found to have a good performance in strengthening polymer compounds [6, 7, 8]. Generally, the plant-derived fiber strength and stiffness were majorly dependent on its content and structures, however, all naturally derived fibers were commonly made up of lignin matrix embedded lignocelluloses fibrils [9].

Adhesion of fiber-matrix is considered one of the leading issues that affect bio-composites-related behavior; accordingly, various approaches have been put forward to solve this issue [6]. Alkali treatment has been gaining much attention due to its effectiveness as a technique for fiber-matrix interfacial bonding improvement that should thus improve the composite behavior [7]. The alkaline treatment solution generally reacts with the fibers' hydroxyl groups to enhance its hydrophilic properties, based on the fact that natural-derived fibers hydrophilic property reduces the mechanical properties and the bonding strength between fibers and the surrounding matrices, leading to better fiber-matrix bonding [9, 10]. In addition, treatment with alkaline solvent resulting in fiber fibrillation such as fiber bundles splitting into fibers to increase fibers surface area for better and more contact with the surrounding matrix [7]. Moreover, seawater was chosen because it is one of the most practical, feasible, and economic implications used to treat the fibers. The observed increase in seawater use could be attributed to its role in removing the hemicellulose and pectin outer layer which is normally protecting the fiber from degradation by weather and higher temperature. This layer is weakly attached to the second layer that is composed of crystal celluloses alongside with lignin and it also leads to fiber fibrillation [11- 13].

The SPF is attracting widespread interest due to its high variety of applications including the paintbrush, pure water filter, broom, septic tank filter base, mop, rope, fish nest hatch eggs, carpet, chair or sofa cushion [7]. The value of sugar palm lies mainly in its high durability and higher resistance to seawater [12, 13]. Furthermore, SPF does not need any additional procedures such as mechanical preparation or water retting to yield the fibers. In thermal and tribology composites, SPFs high content of silica promotes its utilization [11].

Sugar palm fibers have considerable interest in terms of its ability to reinforce composites with other polymers [2]. Preliminary studies of SPF considered it to have tensile strength and a modulus of 173.9 MPa and 3.85 GPa, respectively. Its cellulose content is nearly between 37.3 and 66.5%, the lignin content of 17.9–46.4%, and hemicellulose 4.7– 20.6% [8]. SPF has a common setback like other natural fibers regarding its polymer matrix compatibility, and most of the natural-derived fibers reinforcing properties of polymer related composites are mainly related to the extent of interfacial adhesion between the hydrophobic parts of the polymers and hydrophilic parts of the natural-derived fibers [5].

The present paper aims to validate the effect of seawater and alkaline treatments on the single fiber tensile properties through the effect of two types of treatments on SPF. Seawater and an alkali solution were used to treat the fibers before testing. Single fibers were soaked in seawater for two periods; 15 days (SF-15) and 30 days (SF-30) [12]. Furthermore, the treatment with an alkaline solution was also used with two concentrations; 0.5% and 0.25% for 4 hours and the fibers were labeled as (AF-0.5) and (AF-0.25), respectively [10]. Additionally, the untreated fibers (UF) were examined for comparison purposes as well. An electron microscope scanning (SEM) was used to assess the morphological analysis of the longitudinal and cross- sections of the fibers.

Materials and Method

Materials

SPFs (see Figure 1) were obtained from Negeri Sembilan, Kampung Kuala Jempol, Malaysia local resources. These fibers were black in color, durable, tough, with reasonable seawater resistance [12]. Raw fibers were cleaned followed by a complete washing with the running water to eliminate the probable impurities and dead fibers. Figure 1(a) depicts the sugar palm tree that a sample was taken during the study, while Figure 1(b) shows a bundle of the fibers.

Fig. 1: Sugar palm plant (a) Sugar palm tree (b) Sugar palm bundle.

Single Fiber Test

Diameter Measurements: Diameter measurement of 20 single fibers was performed before the tensile test of every single fiber. SPF cross-sectional view is proposed to have a circular shape as in Figure 2(a). Therefore, further use of the electronic microscope is needed to assess the fibers related diameter. Several measurements were made at several locations within the fibers gauge length as presented in Figure 2(b) and the average diameter was calculated.

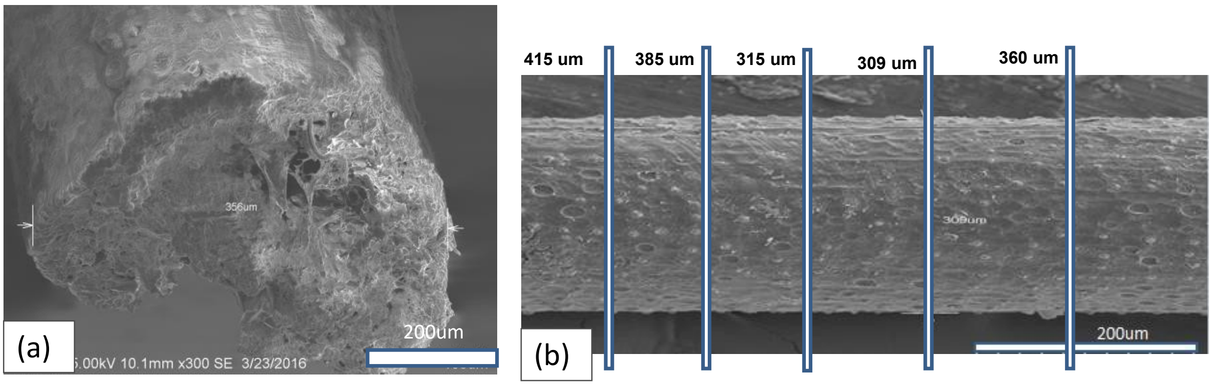

Fig. 2: SEM images of sugar palm fiber (a) Cross-section (b) Longitudinal section.

Single Fiber Tensile Test: A tensile type of test is considered as a simple way to measure the mechanical natural fibers strength. SPF tensile properties were measured using a universal testing machine; Instron Model 5556, as shown in Figure 3(a). ASTM D3379 standard was used for single fiber tensile testing [14]. The scale length of the SPF samples was 20 mm, and the crosshead velocity was 1 mm / min with a 5 kN load cell. The fibers were properly selected under a light microscope before being tested to ensure that the sample gives an accurate result. The fibers were affixed to the sample holder as shown in Figure 3(b) before starting the test, the sample holder was cut in half. Twenty sugar palm fiber samples were prepared for each type of the treatment to performed tensile tests. Figure 3(c) displays the shape of the sample appears after making the tensile test.

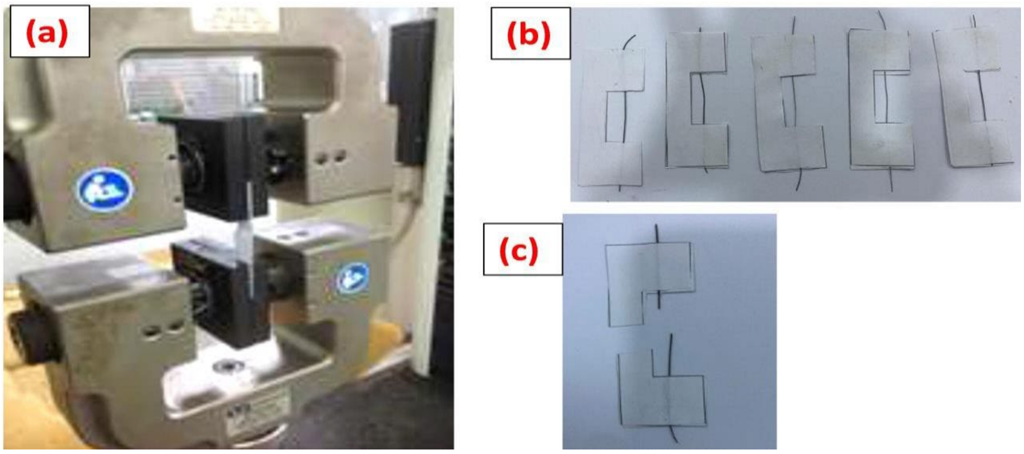

Fig. 3: Single fiber test (a) Single fiber tensile tester (b) Specimens before the test (c) A specimen after the test

Fiber Treatment

Seawater Treatment: Seawater solvent was collected 200 meters from the shore at Port Dickson, Negeri, Sembilan, on the peninsula of Malaysia [10], with pH of 8.32, salinity 3.05%. The SPFs were immersed in the seawater for 15 days (SF-15), and 30 days (SF-30). Then, the fibers were washed with tap water and then allowed to dry. The room temperature ranges from 27.5 to 32.4 °C and 71% R.H.

Alkaline treatment: The SPFs were soaked with two concentrations of the alkaline solution of 0.5% and 0.25% for 4 hours, and the samples were labeled as (AF-0.5) and (AF- 0.25), respectively [10]. The alkaline concentration adjustment is performed by water in addition to a precise amount of the NaOH. Following the SPFs chemical treatment, they were washed lightly using distilled water, followed by an oven-dried process at 80 °C for 24 h to achieve complete removal of any moisture [12].

Morphological analyses (SEM): Morphological types of investigations for the untreated and treated SPFs were performed. SEM (Hitachi S-3400N model) was also performed to assess SPF surface and cross-section at a voltage of 15 kV. A thin layer of gold was used to cover the sample to provide an electrical conductivity, which has a significant effect on image resolution.

Results and Discussion

Single fiber test: Figure 4 shows typical stress-strain curves for SPFs obtained before and after treatments. The SPFs (UF, AF-0.5, SF-15, AF-0.25, and SF-30) were used for a single fiber test, and stress- strain behavior was presented in Fig.4. The trend indicated that the stress elevates linearly with strain values increase until it reaches a particular stress limit; then nonlinear behavior is commonly observed for all study curves [3, 13], Where strain elevates at low-stress limit before failure. These irregular curves indicate that some properties of the fiber are different from each other specifically at the fiber of UF were a significant lower in tensile strain was found. This might be because of the presence of dirt and silica on the outer surface, and because it is also able to absorb moisture and water vapor [13]. Thus, the properties are not proven when used as a reinforcement material with polymers in composites.

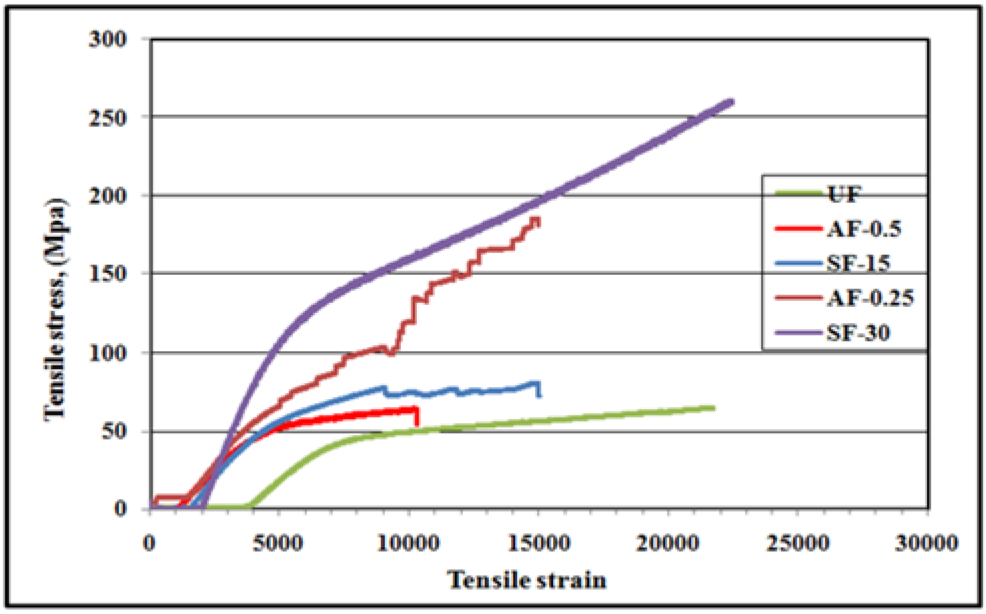

Fig. 4: Stress-strain curves of single SPF test

Figure 5 displays the maximum tensile stress of the single fiber test of treated and untreated SPFs versus the type of treatments. The untreated SPF dominated the worst values of single fiber tensile values. The figure clearly shows that the UF exhibited lower tensile properties than the treated fibers ones. This might belong to the rough and stiff outside surface [11]. Besides, the open ends of the micro-fibers which absorb the moisture from the surroundings are also diminished the properties [15]-17]. This is clearly shown in the morphological images as mention in the next section.

The SF-30 gave the highest average tensile strength of 250 MPa. The long soaking period of the fibers in seawater for 30 days helped peel off the fiber well, removed all the dirt, and made the fiber more elastic [13]. As a result, this means good tensile stress and it will improve the fiber's behavior overall. On the other hand, soaking the fibers for 15 days seemed to be not enough effective to clean the impurities completely. Therefore, these fibers do not display an effective improvement for single fiber properties.

In terms of alkaline treatments, the results depict that the treatment solution also helps to remove the rough outside surface and wax. Moreover, it helps to resolve and reduce the content of hemicellulose and lignin in the fiber structure. This means an increase in the cellulose content percentage which improves the behavior of the fibers [8]. However, the high percentage of the alkaline concentration might damage the fiber structure and break the micro-fibers [10]. It might be suggested that this is the reason for the low tensile properties of the fiber treated with a high concentration of the alkaline solution (AF-0.5) than of the one treated with less concentration (AF-0.25). The properties of sugar palm fibers improved significantly, as the effect of AF-0.5 improved on properties by 10% and then improved SF-15 by 20%, then AF-0.25 by 176%, and the highest effect on sugar palm fibers was SF-30 by 273%.

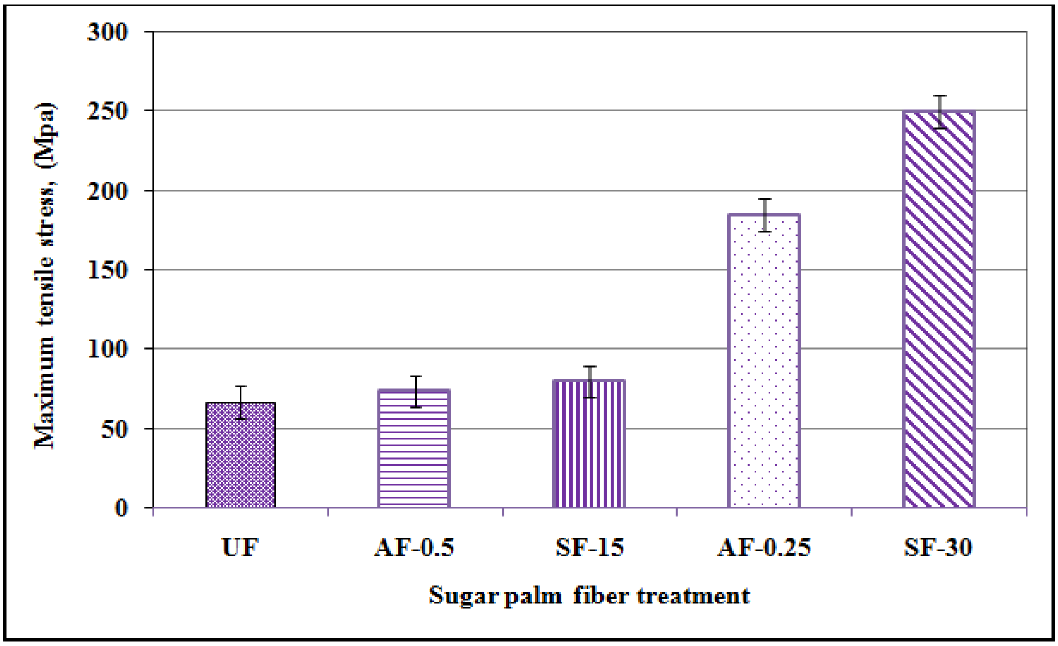

Fig. 5: Tensile stress versus SPF treatments

Morphology Analysis (SEM)

Morphological analyses of the untreated and treated SPFs were performed. The morphology structure of the cellulose fiber is one of the important factors that influence the physical and mechanical properties of the fiber when used as a reinforcing material for polymer composites. From Figure 6 (a), the cross-section clearly shows that a single fiber is made up of a group of fibril and its ends are open (see Figure (6) b). This means its ability to absorb water and moisture is high, which leads to the swelling of the fibers, damage to the superposition, and weak properties. Figure 6 (c, d) of the longitudinal section shows that the outer surface is rough and contains dirt and wax. The thick and rough outlier prevents fiber adhesion with the polymer from being used as a reinforcing material. Subsequently, the bond between it and the matrix is weak, which causes overlapping failure [16, 17].

Figure 7 shows the SEM resulted in images of the alkaline treatments of each single sugar palm fiber. The alkaline solution as seawater as well works on peeling the fibers, cleaning the outer surface, and also removing hemicellulose. Figure 7 (a, b) shows the effect of AF-0.25 fibers on sugar palm fibers in longitudinal and cross-section, as its properties improved. The reason is that alkaline helps to get rid of the hard outer crust and the existing wax and reduces the percentage of silica on the outer surface and reduces the hemicellulose levels. Thus, the properties of the fibers will improve [7, 18].

On the other hand, Figure 7 (a, b) shows the effect of AF-0.5 fiber on SPF in longitudinal and cross-section, as its properties improve as well. The alkaline solution plays the same role and removes the rough outer surface and impurities. Moreover, the high concentration of alkaline solution leads to remove most of the silica on the outer surface and minimize hemicellulose percentage [11]. However, this high concentration ratio affected the mechanism of the cellulose structure. It is broken down cellulose, which is the main column for the properties of lignocellulose fibers which result in reducing single fiber strength. Besides, from the cross-sections of the two types of concentrations, it's clearly shown that the treatment helped to close the ends of the fibril which enhanced fiber behavior.

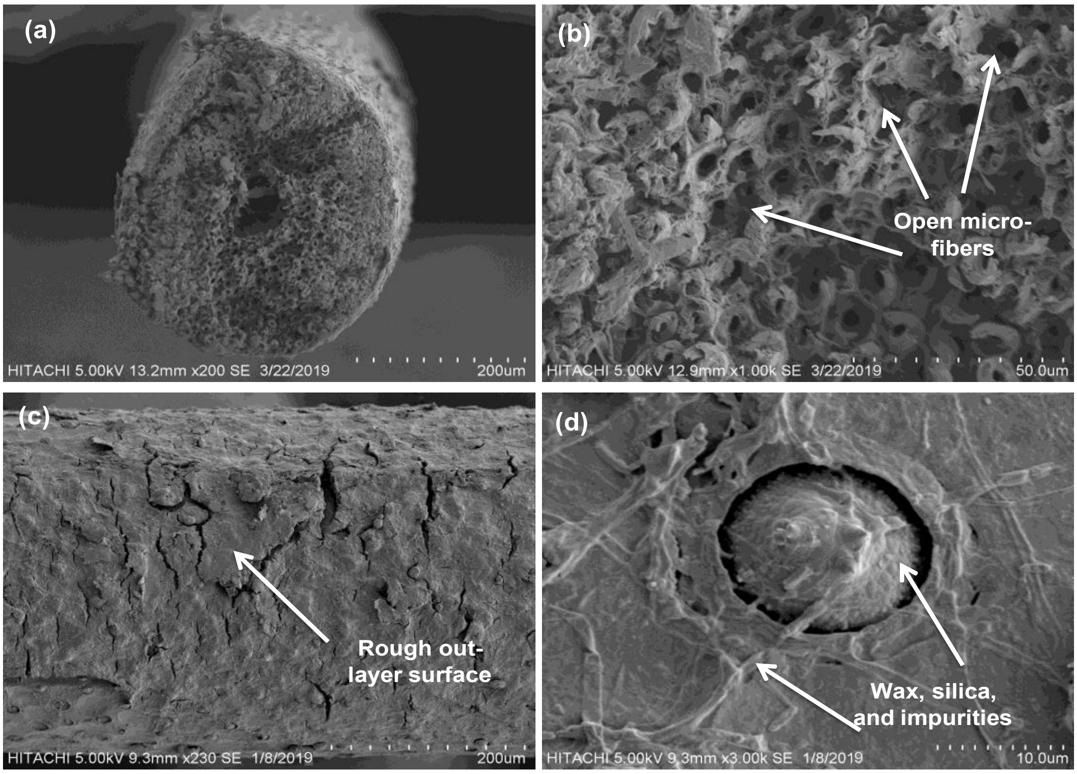

Fig. 6: SEM images of untreated single SPF (a) Cross section (200 um) (b) Cross-section (50 um) (c) Longitudinal section (200 um) (d) Longitudinal section (10 um).

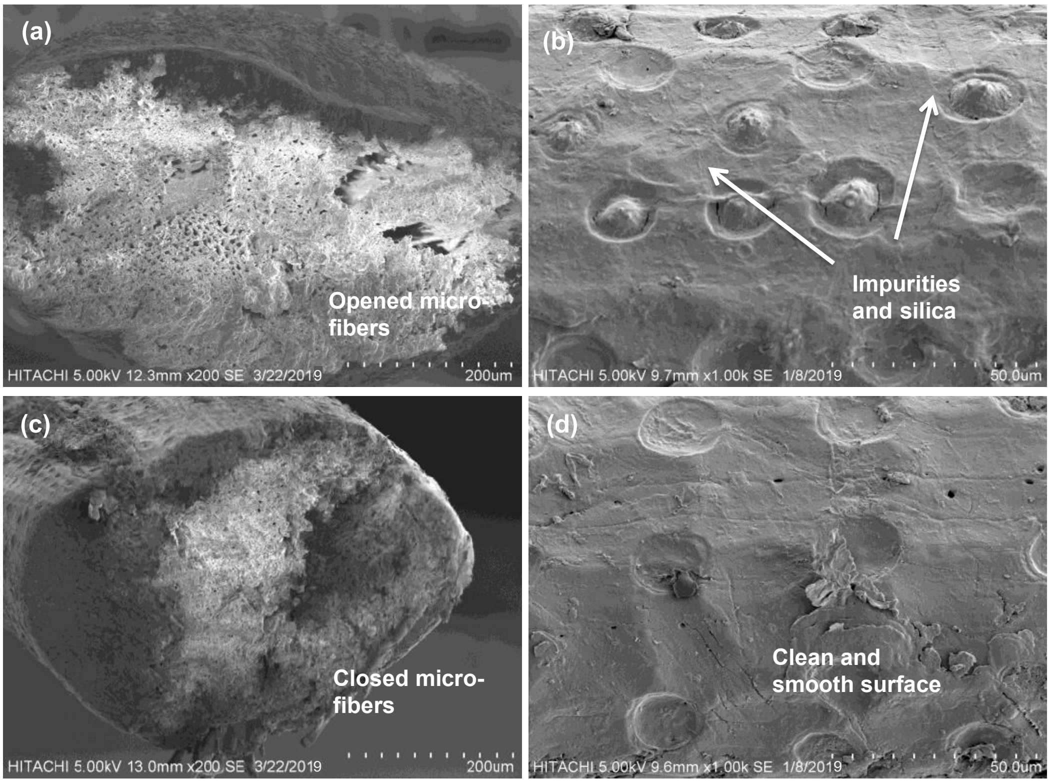

Fig. 7: SEM images of alkaline sugar palm treatment (a) AF-0.25 (cross-section) (b) AF-0.25 (Longitudinal section) (c) AF-0.5 (cross-section) (d) AF-0.5 (Longitudinal section)

Figure 8 shows the effect of seawater on the morphology surface of SPFs. Figure 8 (a and b) shows the effect of the segment the occasional and longitudinal of the SPF with SF-15 fiber, where soaking with seawater for 15 days helped peel off the fiber and got rid of dirt on the SPF, but there is minute dirt that was not eliminated during this period. Figure 8 (c and d) shows the effect of the segment the occasional and longitudinal of the SPF with SF-30 fiber, where soaking with seawater for 30 days helped to clean the fibers from the outer layer, and the smooth surface became clean and the outer fibers were clean, which helped to adhere to the polymer when it was used as a reinforcing material. Whereas, soaking the sugar fibers in seawater for 30 days is better than cleaning for 15 days because it removes the fine dirt from the outer layer of the fiber. It has become completely clean and able to adhere to the polymer when it is used as a strengthening material [16, 18].

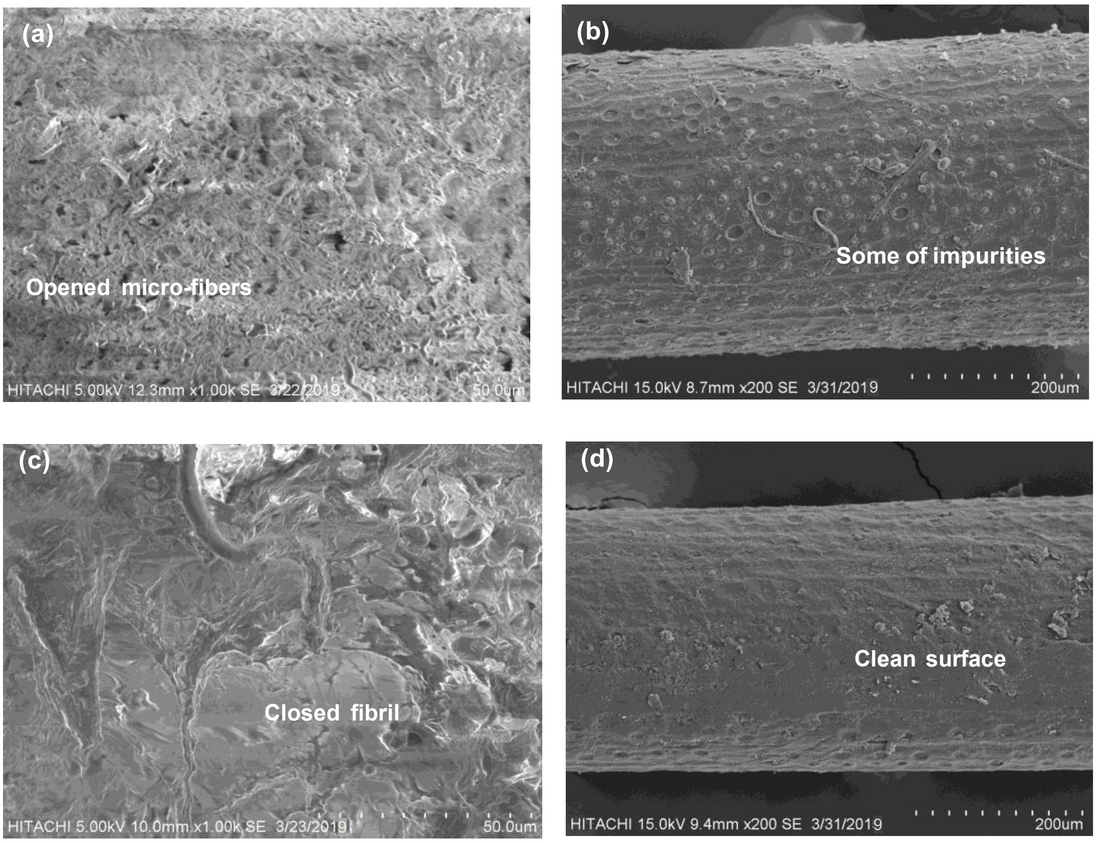

Fig. 8: SEM images of SPF seawater treatment (a) SF-15 (cross-section) (b) SF-15 (longitudinal section) (c) SF-30 (cross-section) (b) SF-30 (longitudinal section)

Conclusions

This research aimed to improve sugar palm fibers properties by soaking them in seawater and alkali treatments. The effect of both treatments was evaluated using the single fiber test and morphological characterizations. These fiber surface treatments help to remove the impurities providing better tensile behavior of the fibers, indicated a significant improvement in the properties of sugar palm fibers, as the effect of AF-0.5 improved on properties of 10%, SF-15 by 20%, AF-0.25 by 176%, and the highest effect on sugar palm fibers was SF-30 by 273%. Finally, it is highly recommended to treat the fibers before using them in the polymer composites.

Acknowledgement

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References

[1] R. M. Shahroze, M. Chandrasekar, K. Senthilkumar, T. Senthilmuthukumar, M. R. Ishak, and M. R. M. Asyraf, "A review on the various fibre treatment techniques used for the fibre surface modification of the sugar palm fibres," Semin. Enau Kebangs., 2019.

[2] A. M. N. Maisara, R. A. Ilyas, S. M. Sapuan, M. R. M. Huzaifah, N. Mohd Nurazzi, and S. O. A. Saifulazry, "Effect of fibre length and sea water treatment on mechanical properties of sugar palm fibre reinforced unsaturated polyester composites," Int. J. Recent Technol. Eng., 2019.

[3] N. Razali, M. S. Salit, M. Jawaid, M. R. Ishak, and Y. Lazim, "A Study on Chemical Composition, Physical, Tensile, Morphological, and Thermal Properties of Roselle Fibre: Effect of Fibre Maturity," Bioresources, vol. 10, no. 1, pp. 1803–1823, 2015.

[4] M. R. M. Huzaifah, S. M. Sapuan, Z. Leman, and M. R. Ishakc, "Comparative study of physical, mechanical, and thermal properties on sugar palm fiber (Arenga pinnata (Wurmb) Merr.) reinforced vinyl ester composites obtained from different geographical locations," BioResources, 2019.

[5] A. Atiqah, M. Jawaid, S. M. Sapuan, and M. R. Ishak, "Physical properties of silane-treated sugar palm fiber reinforced thermoplastic polyurethane composites," IOP Conf. Ser. Mater. Sci. Eng., vol. 368, no. 1, 2018.

[6] S. Mohd Izwan, S. M. Sapuan, M. Y. M. Zuhri, and A. R. Mohamed, "Effects of Benzoyl Treatment on NaOH Treated Sugar Palm Fiber: Tensile, Thermal, and Morphological Properties," J. Mater. Res. Technol., Apr. 2020.

[7] D. Bachtiar, S. M. Sapuan, E. S. Zainudin, A. Khalina, and K. Z. M. Dahlan, "The tensile properties of single sugar palm (Arenga pinnata) fibre," IOP Conf. Ser. Mater. Sci. Eng., vol. 11, no. 1, p. 012012, 2010.

[8] M. R. Ishak, Z. Leman, S. M. Sapuan, M. Z. A. Rahman, and U. M. K. Anwar, "Effects of impregnation pressure on physical and tensile properties of impregnated sugar palm (Arenga pinnata) fibres," 2011.

[9] H. Y. Sastra, J. P. Siregar, S. M. Sapuan, and M. M. Hamdan, "Tensile properties of Arenga pinnata fiber-reinforced epoxy composites," Polym. - Plast. Technol. Eng., 2006.

[10] D. Bachtiar, S. M. Sapuan, and M. M. Hamdan, "The effect of alkaline treatment on tensile properties of sugar palm fibre reinforced epoxy composites," Mater. Des., vol. 29, no. 7, pp. 1285–1290, 2008.

[11] B. Rashid, Z. Leman, M. Jawaid, M. J. Ghazali, and M. R. Ishak, "Physicochemical and thermal properties of lignocellulosic fiber from sugar palm fibers: effect of treatment," cellulose, vol. 23, no. 5, pp. 2905–2916, 2016.

[12] Z. Leman, S. M. Sapuan, M. Azwan, M. M. H. M. Ahmad, and M. a. Maleque, "The Effect of Environmental Treatments on Fiber Surface Properties and Tensile Strength of Sugar Palm Fiber-Reinforced Epoxy Composites," Polym. Plast. Technol. Eng., vol. 47, no. 6, pp. 606–612, 2008.

[13] H. Mardin, I. N. G. Wardana, W. Suprapto, and K. Kamil, "Effect of Sugar Palm Fiber Surface on Interfacial Bonding with Natural Sago Matrix," vol. 2016, 2016.

[14] J. B. Hurst, W. S. Hong, M. L. Gambone, and J. R. Porter, "ASTM single fiber room temperature test standard development," 1998.

[15] M. R. Rashid, B., Leman, Z., Jawaid, M., Ghazali, M.J., Ishak, B. Rashid, Z. Leman, M. Jawaid, M. J. Ghazali, and M. R. Ishak, "Influence of Treatments on the Mechanical and Thermal Properties of Sugar Palm Fibre Reinforced Phenolic Composites," Bioresources, vol. 12, no. 1, pp. 1447–1462, 2017.

[16] S. Misri, Z. Leman, S. M. Sapuan, and M. R. Ishak, "Mechanical properties and fabrication of small boat using woven glass/sugar palm fibres reinforced unsaturated polyester hybrid composite," IOP Conf. Ser. Mater. Sci. Eng., 2010.

[17] Z. Leman, S. M. Sapuan, a. M. Saifol, M. a. Maleque, and M. M. H. M. Ahmad, "Moisture absorption behavior of sugar palm fiber reinforced epoxy composites," Mater. Des., vol. 29, pp. 1666–1670, 2008.

[18] J. Sahari, S. M. Sapuan, Z. N. Ismarrubie, and M. Z. A. Rahman, "Comparative study of physical properties based on different parts of sugar palm fibre reinforced unsaturated polyester composites," 2011.

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Development of Mechanized System for Production of Date-Palm Jaggery Granules

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Keywords: Date-Palm, Jaggery, Sugar product, Traditional process, Jaggery granulator

Abstract. Making of date-palm jaggery (popularly known as *khejur gur*) with its characteristic aroma and flavor is very popular all over India for making various sweet dishes and confectionery products. It is available only for a short duration between middle of November and end of January. The production of solid jaggery includes sap collection (juice) by tapping, filtration, concentration by boiling, cooling of concentrated juice followed by moulding, drying, and storage. Making date-palm jaggery from the raw juice is an art and requires some skill to get the characteristic aroma bearing product with optimum stickiness and colour. Solid jaggery deteriorates rapidly and becomes liquid within 1 or 2 weeks due to its moisture content, invert sugar, and hygroscopic nature. Granular jaggery having low moisture content (1 - 2%d.b) is very popular, tenders several advantages, such as extended shelf-life, easy handling and distribution, high demand for domestic and international markets. It could be made from either solid jaggery or concentrated juice. Therefore, a manually-powered operated granulator (20 kg capacity) was designed, developed, and tested with 5 levels of moisture content (8.4 to 16.25 %db) and 5 levels of rotational speed (48 - 132 rpm) of blades for the production of desired size of jaggery granules. The mass mean diameter of the particles varied linearly with the moisture content of the feed, yielding particles having an average size of 656 µm (D_p) for feed containing 8.4 (%db) moisture. The mean particle size was as low as 700 µm when the machine was operated at 132 rpm with feed moisture content of 12 (%db). The average particle size of 1000 µm is obtained at feed moisture content of 9.0 (%db) and the agitator rotational speed of 76 rpm.

Introduction

Jaggery is a natural sweetener, popularly known by various names such as Gur, Gud, Bellam, and Vellum in different parts of India, and is prepared all over the world under different names. Jaggery forms a key component of the Indian diet, which is either directly consumed or used in making sweet confectionery products. A variety of ayurvedic / traditional medicines are prepared using jaggery [1]. The micronutrients in jaggery have antitoxic and anti-carcinogenic properties [2]. Dietary intake of jaggery can prevent atmospheric pollution related toxicity and the incidence of lung cancer [3].

Jaggery is prepared mainly by concentrating the sugarcane juice, followed by transferring the concentrated juice to moulds for solidification on cooling. It is available in the solid form of different shapes (rectangular block & half-round) and in semi-liquid form. However, the juices obtained/collected from palm trees such as Palmyra palm (*Borassus flabellifer* L.), Coconut palm (*Cocos nucifera* L.), Wild date-palm (*Phoenix sylvestris* Roxb.) and Sago palm (*Caryota urens* L.) are also utilised for jaggery making [4]. India produces nearly 6 million tonnes of jaggery annually, which accounts for 70% of the total production in the world; 65-70% of the total jaggery is from sugarcane and the remaining 30% is from palms. The availability of palm *gur* is seasonal and its price is double that of *gur* made from sugarcane.

Palm trees typically thrive in tropical and subtropical regions. Palmyra, coconut and sago palms grow abundantly in the moist coastal regions. In the dry and hot regions, date and, to some extent, palmyra trees grow well [6]. Palm *gur* industry is the most primitive traditional village industry in India [7]. It is roughly estimated that, there are about 18 crore palm trees in the country; 12.59 crores are available for tapping to collect sap. Tapping of the Silver date-palm (*Phoenix sylvetris*) is an age-old practice in rural West Bengal, India. Some palm species can produce sap all the year-round, whereas Silver date-palm produces sap seasonally [8]. The sap of Silver date-palm is a good source of vitamins of the B group and also contains variable amount of ascorbic acid [9].

Date-palm jaggery (popularly known as khejur gur in Bengal) with its pleasant aroma and flavor is very popular all over India for making various sweet dishes and confectionery products. The preparation of solid jaggery involves sap (juice) collection by tapping, its filtration, concentration by boiling, cooling of concentrated juice, followed by moulding, drying, and storage [8]. In general, the quality, storability, and acceptability of jaggery are determined by the quality of the juice used for jaggery preparation and its physico-chemical changes during boiling. Jaggery storage differs from region to region, including storage in earthen pots, wooden boxes, metal drums, etc. Sometimes, without using any container, the heap of jaggery is just covered with cane trash, bagasse, wheat straw, palmyra leaf mat, etc., to protect the jaggery from ambient humidity. Jaggery deteriorates fast and becomes liquid in 1 or 2 weeks because of the presence of moisture, invert sugar and its hygroscopic nature [10]. For good keeping quality, the moisture content of solid jaggery should not exceed 6% and be kept at a relative humidity of 43-61% [10]. It is estimated that, about 5-10% of the stored jaggery gets spoiled every year, leading to a colossal loss to the tune of 800 million rupees. Granular form of jaggery, which could be prepared either from solid jaggery or concentrated juice, is becoming popular due to the ease of its handling, packaging, and storage [11].

The preparation of granular jaggery involves concentration of sap by boiling, cooling, and scrapping of concentrated juice, followed by drying and sieving. The shearing action, which exposes more surface for regulated cooling under atmospheric conditions, is a labor-intensive process. Careful operation at this stage facilitates the formation of uniform lumps and agglomerates (jaggery granules). This is followed by drying the mass under the sun or hot air drying using mechanical dryer or polyhouse dryer up to 1 -2 %db moisture content, sieving, and packing [2]. The process for preparation of granular form of jaggery from either sugarcane or palmyra-palm (Panela pulverizada, Muscovado, and sucanat) in other countries is a similar sequence of manual operations. In the traditional process of granular jaggery, simultaneous cooling and scrapping of concentrated semi-solid mass to prepare granules is a vital operation.

Solar energy for evaporation of palmyra palm and sugarcane juice was reported by Mathur and Khanna [6]. Engineering properties of sugarcane juice concentrated syrup and jaggery were reported by Pandey [12]; Tiwari et al., have evaluated convective heat and mass transfer for pool boiling of sugarcane juice [13]; Rao et al., have studied moisture sorption isotherms of sugarcane, palmyra and date-palm jaggery [11], thermophysical properties of sugarcane, palmyra-palm and date-palm granular jaggery [14], changes in physical and thermo-physical properties of sugarcane and palm juice [15], the effect of moisture on sticky point and glass transition temperatures of sugarcane, palmyra-palm and date-palm jaggery granules [4] and effect of anti-caking agents on palmyra-palm sorption isotherms [16]. Engineering properties of palmyrah palm jaggery were studied by Nighitha and Sudagar [17]; Deotale et al. studied the storage behaviour of solid and liquid forms of sugarcane and palm jaggery [18]. The information on development of mechanized jaggery granulator is scanty. The present investigation was aimed at development of manually-cum-power operated granulator to replace slow, unhygienic, and labor-intensive manual operation and was evaluated at different levels of moisture content and rotational speeds for the production of uniform sized granules.

Materials and Methods

Development of Jaggery Granulator

In the conventional process of granular jaggery, simultaneous cooling and scrapping of semi - solid mass to get the desired size of granules is a vital operation. The concept of simultaneous cooling and scrapping has been adopted to mechanise this process. The scrapping operation could be achieved with slow agitation of the semi - solid mass. A manually cum power operated granulator has been designed and developed with a capacity to handle 20 kg pasty jaggery (around 81% w/w Total Soluble Solids (TSS) and temperature around 90ºC).

Components of the Jaggery Granulator

Figure 1 represents the front view of the jaggery granulator. The inner dimensions of the machine are as follows: width = 300 mm, depth = 300 mm, length = 350 mm. It was made with 8 mm thick mild steel plate. The trough holds 20 kg of concentrated mass upto the height of 140 mm from the bottom. The main shaft is fixed along the length of the vessel, at 150 mm from the bottom, with suitable water-seal bearings at two ends. Along the main shaft, blades (agitators) are placed at 120º. The blades are not in the same plane, rather welded to the shaft in a staggered position. These blades are also not vertically placed. They are aligned at 30º with the shaft (Fig. 1). Altogether, there are 23 blades along the total length of the shaft. The blade to blade distance in a row on the main shaft is 26 mm, while at the ends, the distance between the blade and the surface of the vessel is 27 mm. When the shaft is turned, the bottom blades initiate agitation in upward direction, and top blades at the other end starts pushing the mass downward. The shaft is provided with a handle to rotate the agitator. Chain and sprocket drive mechanism is adopted for power transmission to the shaft (agitator blades) through a motor. The vessel has an outlet (75 mm) provided with a removable door to discharge granular product. The whole assembly is fixed on MS frame (545 ×625 ×700 mm) fitted with wheels for easy shifting of the machine. The vessel is also provided with a water jacket for circulation of cold water which facilitates the controlled cooling of the mass during agitation. A wire screen door is provided at the top of the vessel (324 × 366 mm) to prevent entry of any undesirable material in the mass as well as to protect the operator from any accident with the rotating blades.

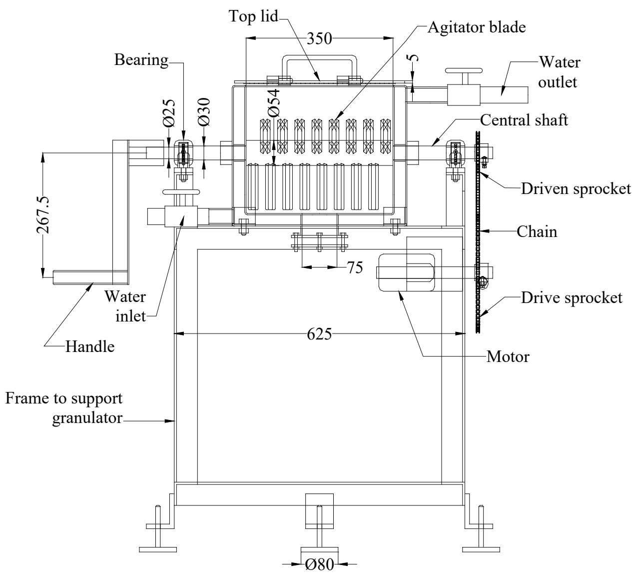

Fig. 1 Front view of the jaggery granulator

Performance Evaluation of the Jaggery Granulator

Raw material

Collection of juice from date-palm tree

Early in the morning, sixty litres of juice were collected from various date-palm trees in Kharar village (22.4102° N, 87.8631° E), East Midnapur district, West Bengal, India.The agro-climatic conditions of this area are suitable for cultivating date-palm trees.

Preparation of concentrated juice

After collection of juice from the date-palm tree, juice was first filtered through a fine muslin cloth, and boiling was carried out in an open, shallow aluminium pan having surface area of about 0.81 m^2 and depth of liquid was 0.15 m. The juice was heated using traditional furnace constructed with locally available mud bricks and clay and fuels such as leaves and straw were used to supply energy for boiling. Boiling of juice was continued about 2 h 40 minutes during which, the froth and scum was removed from the surface periodically using suitable ladle. The boiling of the juice was controlled by sprinkle water over the juice, otherwise, the juice, along with froth, spill over the boiling pan and care was taken to avoid charring the juice. Finally, the required concentration level was judged manually by cooling an aliquot of syrup dropped in water and the solidification of mass was considered as striking point at which the concentrated juice was collected and used for testing of jaggery granulator (Fig.1).

Temperature and TSS of juice during concentration

For each of the processes, juice temperature during boiling was measured periodically at regular intervals using thermocouples (copper- constantan) coupled to a digital temperature indicator (−50 to 200°C) with resolution of 0.1°C. Samples were collected at regular intervals to determine the TSS (% w/w) using three portable refractometers (Models 0–32, 28–62 and 58–92 °Brix, Erma Optical Works Ltd., Tokyo, Japan) having a resolution of 0.1°Brix (% w/w) for each.

Testing of the Granulator

A manually cum power operated granulator to handle 20 kg pasty jaggery (around 81% w/w concentration and at 90ºC) has been developed (Fig.1) and tested with concentrated juice of date-palm at 5 levels of moisture content (8.4 to 16.25 %db). The agitator blades were rotated at fixed rpm (48 - 132 rpm; 5 levels) for 15 minutes. The wet granules were discharged and allowed to dry up to a moisture content of 1.5 - 2 %db on a tray dryer at 50ºC and air flow rate of 2 $m.s^{-1}$. Optimum moisture level and rotational speed was arrived to get desired D_p of the particle.

Experimental design

Two independent variables, like moisture content (M, %db) and agitator speed (N, rpm), were considered to be important for obtaining jaggery granules of desired quality. The levels and code values of these independent variables are given in Table 1.

Table 1 Levels and codes of independent variables in evaluation of the granulator

Factors	Coded factor	Coded values				
		-1.414	-1.0	0.0	+1.0	+1.414
Moisture content (M, %db)	M	8.000	9.0	12.0	15.0	16.500
Agitator speed (N, rpm)	N	31	48	90	132	149

The second order Central Composite Rotatable Design (CCRD) (Response surface, two factor, Quadratic, polynomial model) suggested thirteen experiments with two variables and five levels of each variable in three replications [19,20]. The independent parameters for evaluation are moisture content of concentrated mass (M, %db) and speed of the agitator blades (N, rpm) (Table 2). For each combination of the independent variables in the experimental design, the dependent variable of the granular jaggery is mass mean diameter of the particle.

Table 2 Actual and coded values of variables M (%db) and N (rpm) in the CCRD Design for the testing of jaggery granulator

Experiment No.	Moisture content ,M (%db)		Agitator Speed, N (rpm)	
	Coded	Actual (%db)	Coded	Actual (rpm)
1	0	12.15	0	90
2	+1.414	16.30	0	90
3	−1.414	7.70	0	90
4	0	12.15	0	90
5	0	12.15	0	90
6	+1	15.40	+1	132
7	0	12.15	+1.414	149
8	0	12.15	0	90
9	0	12.15	0	90
10	−1	9.20	+1	132
11	+1	15.40	−1	48
12	−1	9.20	-1	48
13	0	12.15	−1.414	31

The correlations between the independent variables and the mass mean diameter of the granular jaggery were obtained following linear and non-linear regression techniques.

Optimization

Optimization of various parameters has been analyzed with Design-Expert Version 13.0 [21]. Design-Expert numerical optimization will maximize, minimize, or target a single response (or) combination of two or more responses. The programme uses five possibilities (None, Maximize, Minimize, Target, In range, and Equal to) for a "Goal" to construct desirability indices. Desirability varies from zero to one for any given response. The programme combines the individual desirability into a single number and then searches for the greatest overall desirability. A value of 'one' represents the ideal case and a 'zero' indicates that one or more responses fall outside the desirable limits.

Moisture content of samples

The moisture contents of each equilibrated jaggery sample (in triplicate) were determined by vacuum oven drying method [22], and mean values were noted.

Particle size distribution

The particle size distribution of the granular jaggery samples (100g each) was determined by sieve analysis technique [23] using different sieves with mesh sizes 0.6, 0.5, 0.25, 0.21, and 0.15 mm. The stack of sieves was vibrated vertically using vibratory laboratory sieve shaker (Fritsch 03.502, West Germany) for 5 minutes at a frequency of 50 Hz. The weight of sample retained on each of the sieves was weighed. All tests were done in triplicate. The mass mean diameter, Dm (µm) of the particles for each jaggery sample was evaluated using equation (1).

$$D_m = \sum_{i=1}^{n} \Delta\phi_i \; D_{pi} \quad (1)$$

Where (µm) is the average size of the two consecutive sieves placed in series, Δ is the weight fraction of the powder retained on the sieves having average diameter, and n is number of sieves used.

Statistical Analysis

Linear and nonlinear regression analysis for correlating various properties of the granular jaggery was carried out with the Microsoft Excel 2013 [24] and Origin 2017 package [25].

Results and Discussion

Performance of the Jaggery Granulator

Effect of moisture content and rotational speed of the agitator blade on particle size distribution in the jaggery granules

Figure 2 shows the particle size distribution of jaggery granules obtained from pasty jaggery fed at different moisture contents when the granulator was operated at 120 rpm. It was noted that, the granulator generated bigger size particles when the moisture content of the feed was increased as evident from higher mass fraction retained on the screen having larger opening. Higher mass fraction (51-70%) of granules retained on screen with larger opening (≥1400 µm) was observed when the moisture content range was 12.15 to 16.25 (%db), while higher mass fraction (29-51%) retained on screen with smaller opening size (< 250 µm) for feed containing minimum moisture content 8.4 - 9.2 (%db). Thus, it revealed that, moisture content in the feed has considerable effect on the particle size distribution in the final product. The change in mass mean diameter of the particles varied linearly with the moisture content of the feed, yielding average size of the particles 656 µm (D_p) for feed containing 8.4 (%db) moisture while it was 1230 µm when the moisture content was 16.25 (%db) (Figure 3).

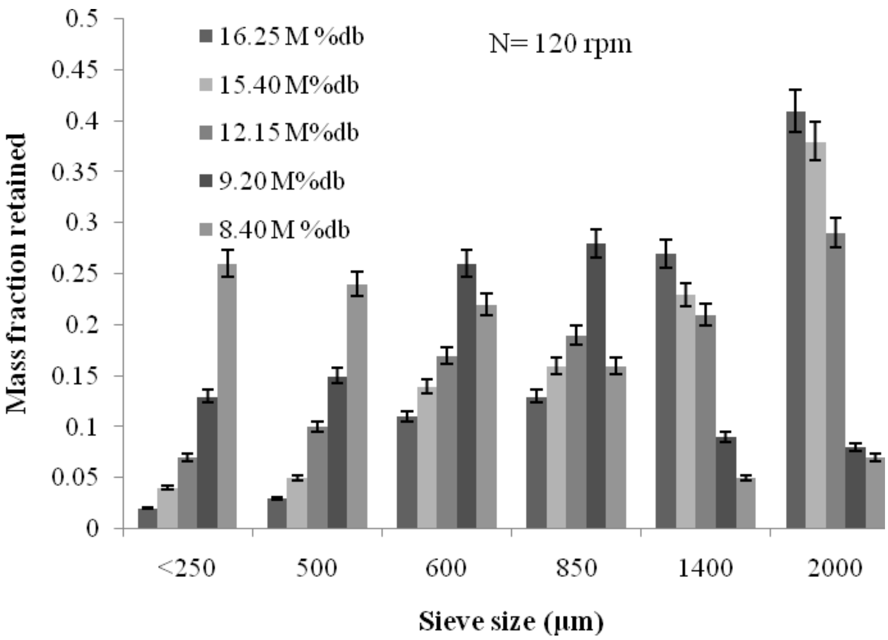

Fig. 2 Effect of moisture content on particle size distribution of granular jaggery

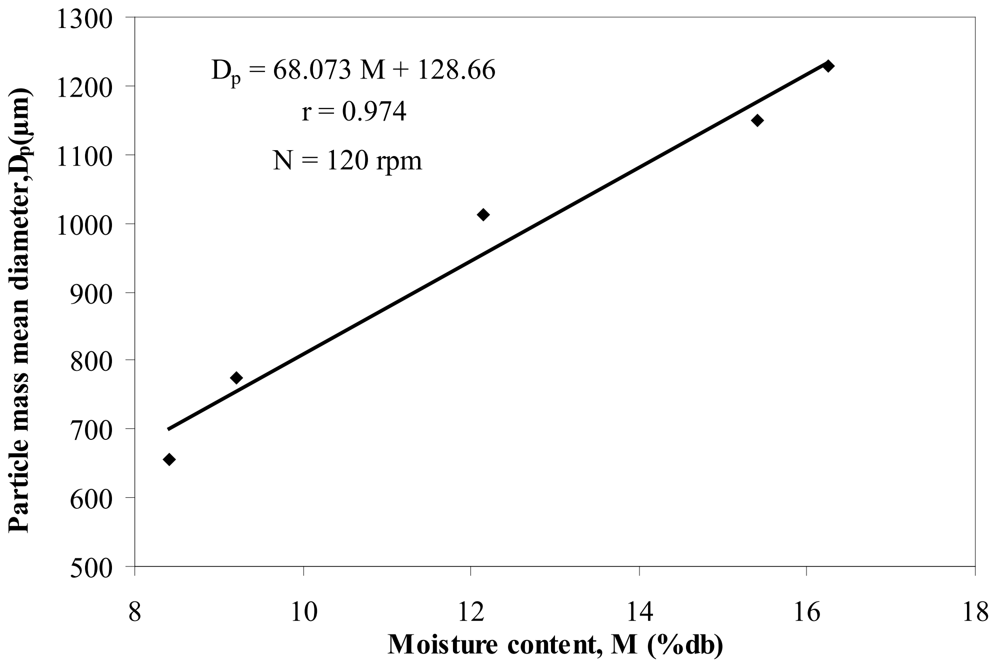

Fig. 3 Variation of mass mean diameter of particles with moisture content of the feed

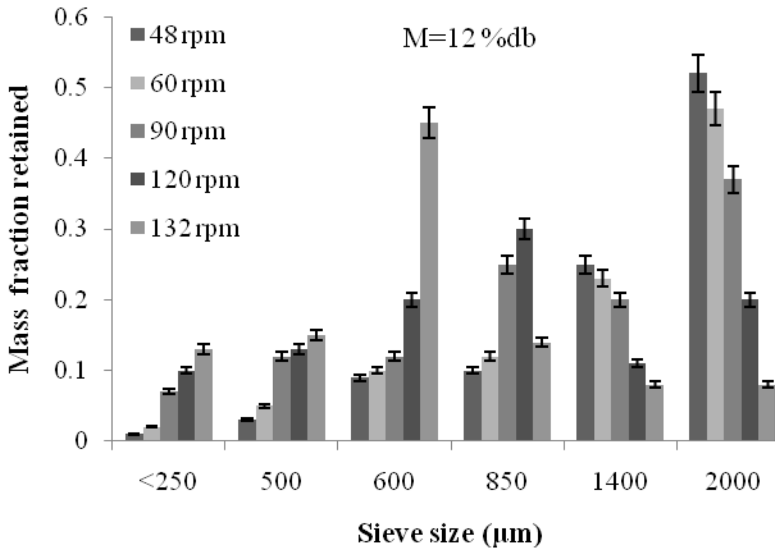

Fig. 4 Effect of rotational speed on particle size distribution of granular jaggery

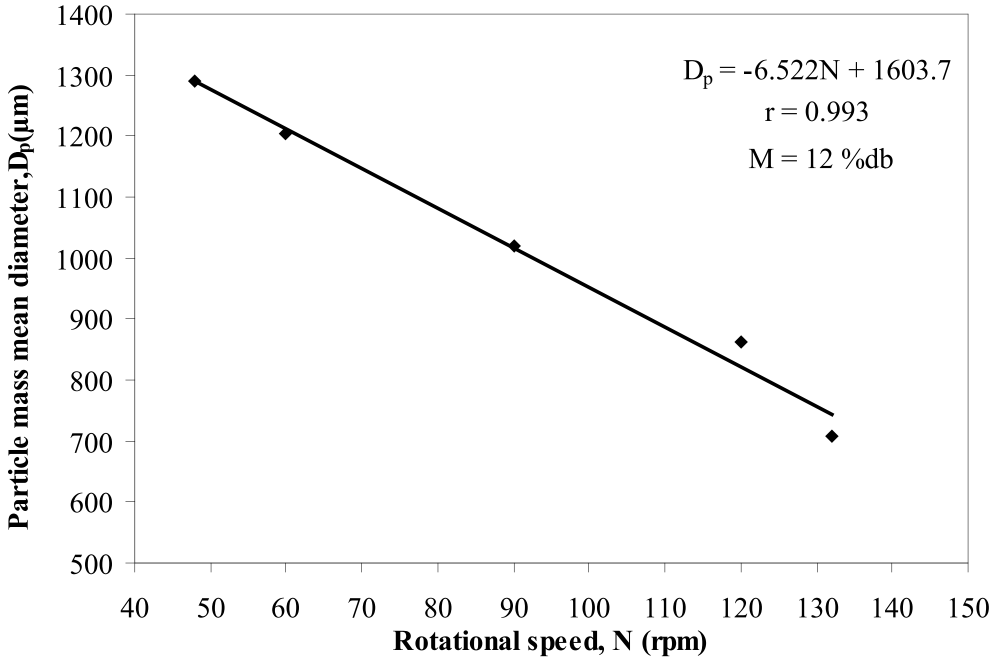

Fig. 5 Variation of mass mean diameter of particles with rotational speed of the agitator blades

Figure 4 further shows that higher mass fraction of particles (76 %) retained on screen with larger opening (≥2000 µm) when the rotational speed was as low as 48 rpm, suggesting generation of larger size particles. However, higher mass fraction (72.5%) of smaller size particles (around 600 µm) was obtained when the rotational speed was as high as 132 rpm. The mean particle size was as low as 700 µm when the machine was operated at 132 rpm and that increased linearly to 1300 µm when the agitator speed was reduced to 48 rpm (Fig.5).

Combined effect of moisture content of the feed and rotational speed of the agitator blade on mass mean diameter of the jaggery granules

Table 3 shows the mass mean diameter of particles obtained with different combinations of independent variables as per the experimental design. Since, the exact moisture content (as per experimental design) could not be achieved, close values to these moisture content of the jaggery granules was considered for optimization analysis. Equation (2) shows the linear correlation among the variables with correlation coefficient of 0.866. Optimum values of moisture content of the feed and rotational speed were presented in Table 4. It is revealed that, moisture content of feed at 9.0 (%db) yields average particle size of 1000 µm when the rotational speed of the agitator is maintained at 76 rpm.

$$D_p = 960.84 + 32.35\,M - 3.33\,N \qquad (r = 0.812) \qquad (2)$$

Table 3 Effect of moisture content of concentrated jaggery mass and rotational speed on mass mean diameter of the particle

Moisture content, M (%db)	Rotational speed, N (rpm),	Particle mass mean diameter (μm), D_p
12.15	90	892
16.30	90	1282
7.70	90	820
12.15	90	894
12.15	90	890
15.40	132	1121
12.15	149	731
12.15	90	1112
12.15	90	1124
9.20	132	1023
15.40	48	1233
9.20	48	1208
12.15	31	1312

Table 4 Optimized values of different parameters for jaggery granulator

Parameters	Optimum value
Moisture content (%db)	9.0
Rotational speed (rpm)	76
Particle mass mean diameter (μm)	1000
Desirability	0.875

Conclusions

A manually-cum-power operated granulator (20 kg capacity) was developed and tested with concentrated juice of date-palm (around 81% w/w concentration and at 90ºC). The moisture content in the feed and rotational speed of blades has considerable effect on the particle size distribution in the final product. Granules with mass mean diameter of 656 μm and 1230 μm are obtained when the jaggery granulator operates with feed containing 8.4%db and 16.25%db moisture content, respectively. Larger mass fraction of smaller size particles (≤ 600 μm) is obtained with maximum rotational speed of 132 rpm. The moisture content of feed at 9.0%db and rotational speed of 76 rpm are found to be optimum for the granulator. It was concluded that, granulator developed in the study can be used for production of uniform size jaggery granules of 1000 μm which helps jaggery farmers to get remunerative price for granular jaggery and eliminates labor intensive operation.

References

[1] Pattnayak, P.K. Misra, M.K. Energetic and economics of traditional gur preparation: A case study in Ganjam District of Orissa, India. Biomass & Bioenergy. 26 (2004) 79-88.

[2] Jagannadha Rao, P.V.K. Madhusweta, Das. Das, S.K. Jaggery- A Traditional Indian Sweetener. Ind. J. Tradit. Knowl. 6 (1) (2007) 95-102.

[3] Sahu, A.P. Paul, B.N. The role of dietary whole sugar- jaggery in prevention of respiratory toxicity of air toxics and in lung cancer. Toxicol. Lett. 95 (1) (1998) 154.

[4] Jagannadha Rao, P.V.K. Madhusweta, Das. Das, S.K. Effect of moisture content on glass transition and sticky point temperatures of sugarcane, palmyra-palm and date-palm jaggery granules. Int. J. Food Sci.Technol. 45 (2010) 94-104.

[5] Vengaiah, P.C. Ravindrababu, D. Murthy, G.N. Prasad, K.R. Jaggery from palmyra palm-present status and scope. Ind. J. Tradit. Knowl. 12 (4) (2013) 714-717.

[6] Mathur, K.N. Khanna, M.L. Application of solar energy to small scale industries. Sol. Energy. 1 (1) (1957) 34.

[7] Das, S. Palm gur industry-Key to rural economy. Orissa Review, (2004)18-20.

[8] http://orissagov.nic.in/e-magazine/Orissareview/Sept2004/englishPdf/sep04.pdf

[9] Bakshi, P. Sinha, A. Basu, D. Indigeneous technical knowledge in processing off date palm juice and its implications on livelihood in Nadia district of West Bengal. J. Crop. Weed. 16(2) (2020) 130-134.

[10] Rangaswami, G. Palm tree crops in India. Outlook. Agric. (UK), 9(4) (1977) 167-173.

[11] Chockalingam, C. Gur manufacture in Tamil Nadu- A review, Proceedings of national seminar-cum-group discussion on jaggery manufacture and storage, Lucknow, 95 (1985).

[12] Jagannadha Rao, P.V.K. Das, S.K. Das, Madhusweta. Moisture sorption isotherms of sugarcane, palmyra-palm and date-palm jaggery. In: Proceedings of American Society of Agricultural and Biological Engineers Annual International Meeting (paper no. 063007), Portland, Oregon, 9-12th July (2006).

[13] Pandey, J. P. Report on engineering properties of sugarcane juice concentrated syrup and jaggery. Department of Process and Food Engineering, Pantnagar, India, (2001).

[14] Tiwari, G.N. Om, Prakash. Subodh, Kumar. Evaluation of convective heat and mass transfer for pool boiling of sugarcane juice. Energy. Convers. Manag. 45 (2004)171-179.

[15] Jagannadha Rao, P.V.K. Das, Madhusweta. Das, S.K. Thermophysical properties of sugarcane, palmyra-palm and date-palm granular jaggery. Int. J. Food. Prop. 11 (2008) 876-886.

[16] Jagannadha Rao, P. V. K. Madhusweta, Das. Das, S.K. Changes in physical and thermo-physical properties of sugarcane, palmyra-palm and date-palm juices at different concentrations of sugar. J. Food Eng. 90 (2009) 559-566.

[17] Jagannadha Rao, P.V.K. Madhusweta, Das. Das, S.K. Effect of anti-caking agents on moisture sorption isotherms of palmyra-palm jaggery granules. Int J Proc Post Harvest Technol. 8 (2) (2017)113-122.

[18] Nighitha, M.T. Sudagar, I.P. Engineering Properties of Palmyra-palm Jaggery. Trends Biosci. 10 (43) (2017) 8974-8976.

[19] Deotale, S. Bhotmange, M.G. Halde, P. Chitale, M. Study of traditional Indian sweetener "Jaggery" and its storage behavior. Int. J. Chem. Stud. 7(3) (2019). 410-416.

[20] Myers, R.H. Response surface methodlogy. Boston, MA: Allyan and Bacon (1971).

[21] Sandanasamy, J. Yusoff, M.M. Gimbun, J. Optimization of Ultrasonic-Assisted Extraction of Polyphenolic and Flavonoids from Labisia pumila. In Materials Science Forum. 890 (2017) 167-170.

[22] Anonymous, Stat-Ease Version 13. East Hennepin Avenue, Suite 480, Minneapolis, MN 55413, USA: Stat-Ease, Inc (2021).

[23] AOAC. Official methods of analysis. Washington DC, USA: Association of Official Analytical Chemists (1998).

[24] Linden, G. Methods of particle size analysis. In Analytical Techniques for Foods and Agricultural Products; Melcion J.P., and Monredon, F.De., (Eds.), VCH Publishers: New York, First Edition, (1996) pp.229-248.

[25] Anonymous, Microsoft Office Professional Edition 2013. Microsoft Office Excel. One Microsoft Way, Redmond, WA 98052-6399, USA: Microsoft, Inc (2013).

[26] Anonymous, Origin. 2017. Non-Linear Curve Fit. Ver.6.1. Northampton, MA 01060, USA: Origin Lab, Inc (2017).

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Characteristics of Liquefied Adhesive Made of Oil-Palm Trunk (OPT) and their Application for Particleboard's Binding

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Abstract. Liquefied adhesive made of oil-palm trunk (OPT) was produced according to bio-refinery concept. In this context, OPT was converted into 20-60 mesh powder and it was converted into liquid via liquefaction process involving reaction of thermo-chemical and resulting in pre-polymer like phenol-formaldehyde (PF). The characteristics were determined based on Indonesian Standard (SNI) 06-4567-1998 for PF resin. The pre-polymer then was used for binding of three composition types of particleboards, namely 100% OPT particle, 50:50 mixture of OPT and jabon wood particles, and 100% jabon wood particle. Evaluation of the board was carried out based on Japanese Industrial Standard (JIS) A 5908-2003 for particleboard. Results of this study exhibited properties of the pre-polymer generally met the SNI except its viscosity was too high. For overcoming this, the pre-polymer was then diluted in solvent until it was appropriate to be placed in spray gun and passed the nozzle for further use as binder. Physical properties of the board showed moisture content (MC) and density fulfilled JIS standard however thickness swelling was up to limit. Mechanical properties of the board showed only modulus of elasticity (MoE) met the criteria of JIS while modulus of rupture (MoR) and internal bonding were below the target. Statistically, two parameters, namely MC and MoE were different among the boards. For sum up, making adhesive from oil-palm stem using bio-refinery method was feasible and it can be applied for particleboard binding.

Introduction

Oil palm (*Elaeis guineensis* Jacq.) is largely cultivated for fruits generating thus resulted in oil production having economic life spans about 25-30 years [1]. The oil is used in a major variety of daily necessity, including edible products such as frying oil, margarine, shortening, emulsifiers, ice creams and confectionary products [2,3], non-edible products such as cosmetics and their derivatives (skin care, lotions, powders, deodorants, perfumes, lipstick, nail polish, face make-up, hair pomade, bath oils and bubbles, infant care products and plenty other types and widespread of products for women), personal care products (soaps, shampoos, creams, and waxes), and households cleaner (detergents, candles and polishes) [4]. In advance, it has been used for supporting industries, such as oleochemicals for producing fatty acid methyl esters, fatty alcohols and glycerine [5], surfactant in petrochemicals for producing plastics, textiles, and lubricant [6], bioenergy for producing biodiesel [7], including medicine for developing pharmaceutical products [8].

These commodities are economically beneficial for income generating particularly in Southeast Asia [9]; therefore, this crop now has been expanded dramatically. Today, this palm is cultivated in 42 countries worldwide [10], with Indonesia, Malaysia, and Thailand accounting for roughly 80% of global oil palm estates [11]. The first two are the world's leading producers of palm oil and oil palm goods, with the world's largest planted oil palm area [12]. Table 1 illustrated their development in a last decade. Both data area harvested and the production of oil palm in the predominant country in Southeast Asia and world a decade back showed increase [13].

Table 1. World area harvested and oil palm production within the predominant three countries in Southeast Asia during 2009-2019; consisting of Indonesia, Malaysia, and Thailand (own elaboration according to [13]

Country	Year	Area harvested (ha)	Production (tonnes)
Indonesia	2009	5,370,000	90,000,000
	2019	14,677,560	245,633,087
Malaysia	2009	4,691,160	85,705,499
	2019	5,216,822	99,065,364
Thailand	2009	510,003	8,162,703
	2019	896,322	16,772,430
World	2009	16,158,445	216,414,772
	2019	28,312,612	410,696,692

Consequently, a huge quantity of biomass residues is generated abundantly in both countries. In oil palm plantations, there are two significant biomass residues: oil palm frond (OPF) and oil palm trunk (OPT), although only OPT was included in this study [14]. For decades, OPF has been utilized as a grass substitute and a source of roughage for ruminants such as goats, beef, and dairy cattle without any reports of toxicity [15] where agricultural locations are typically located near oil palm plantations. Long-term feeding of OPF-based feeds, whether fresh or processed as silage or pellets, has been shown to produce high-quality carcasses and safe meat [16].

Even though there is a vast quantity of OPT available, it has received less attention in studies and research [17]. Only after the palm's economic lifespan has been achieved at the moment of rejuvenation is OPT available. The diameter of the felled trunk ranged from 45 to 65 cm during replanting [9]. Using OPT as a raw material to create value-added products will save production costs while also increasing economic returns [9]. Furthermore, OPT is a non-timber source that is abundant in replanting locations and might be used as a raw material substitute for various items that have traditionally been made of wood [18]. In addition, OPT tends to be converted into advanced materials via bio-refinery concept. Bio-refinery is a potential concept for producing energy, platform chemicals, and materials using biomass or other renewable resources as feedstocks. It is regarded as one of the solutions for reducing carbon footprint and fossil fuel for dependency for long-term growth [19]. In this context, the OPT will be converted into chemicals, hereafter adhesive via liquefaction and also raw material as replacement of wood, hereafter particleboard.

Since its properties are very different from wood, utilization in solid form of OPT is less promising. It is very hygroscopic in the nature; consequently, it raises dimensional instability thus less durable. Many attempts have been done for improving these drawbacks properties by employing whole trunk into products, for example laminated combination using tropical wood [20], engineered composite board [21], or resin impregnated to the trunk [22]. Anatomically, OPT comprised of vascular bundles embedded in parenchyma tissues [23]. The presence both of these parts influences the characteristics further [24], hence some scientists separated between the two prior to further processing and utilized only one part, for instances parenchyma tissue for sugar extraction (glucose and xylose) [25, 26] and generating starch for the manufacture of wood adhesive [27] even though the yield was very limited and depended on position on the stem; bottom, middle, or upper part. Only a few papers, on the other hand, used vascular bundles as raw materials, such as manufacturing composite plastics using a polyethylene matrix [28] and producing oriented strand board (OSB) on a lab scale [29].

Ugovšek et al. [30] examined the use of vascular bundles generated from OPT by a liquefaction process involving a thermo-chemical reaction that produces various bio-copolymers like as coatings, various polymers, carbon fibers, foams, and adhesives. Liquefaction is one method for converting whole biomass into liquids [31]. This research is appropriate since the vascular bundle is a lignocellulose material with a nature similar to wood and a lignin content of up to 22% [32, 33]. Furthermore, according to a recent paper [31], both virgin and waste lignocellulose materials have been successfully converted into wood adhesives. This is the first study to look into using vascular bundles as a raw material for wood adhesives through liquefaction process as well as for manufacturing particleboard. As a result, the goal of this research was to assess the performance of the liquefied adhesive as well as the quality of the particleboard bonded with it.

Materials and Methods

Preparation of the materials

It was reported that machining and sawing properties of OPT was difficult and the quality of finished material was rough because of presence of silica [23]. Therefore, in this work converting OPT was carried out using a planer machine. This machine was capable to alter solid form into particle size in short time. The particles were then submerged in water for 8 hours to separate the vascular bundles from the parenchyma. The vascular bundle will be left in the sieve as a residue, while the parenchyma will be filtered out. The resulting vascular bundles were air-dried, ground to a size of 20-60 mesh, oven-dried for 24 hours at 103+2°C, and stored for future use.

Production of liquefied adhesive

In a beaker glass, a 100 g oven-dry vascular bundle with a moisture content (MC) of 5% was put. 25 mL 98% H_2SO_4 (5% phenol weight) was added and gently agitated for 30 minutes. The liquid was then placed in a sealed beaker glass to condition. After 24 hours, 500 mL liquid phenol (melted in 60°C) was added to the mixture, which was gently stirred until it seemed homogeneous. After adding 40% sodium hydroxide (NaOH) until the pH reached 8, formaldehyde 37% was added using a phenol to formaldehyde (P/F) ratio of 1:1.2. The extract was then cooked in a water bath at 90°C for 2 hours after being filtered using Whatman filter paper number 1. The extract was then preserved in a glass bottle until it was time to use it.

Determination of basic properties of the liquefied adhesive

Determination and evaluation of basic properties of resulted liquefied adhesive were carried out according to Indonesian Standard SNI 06-4567-1998 for phenol-formaldehyde (PF) resin. Performance, specific gravity, solid content, viscosity, pH, gel time, and free formaldehyde were all considered.

The clarity, color, and presence of dust of the liquefied adhesive were observed using either the naked eye or a microscope. Visual inspection of the glue, either with the naked eye or under a microscope, was used to determine its clarity. To generate a film layer, a sample of the adhesive was put onto a petri dish or a glass slide. Color and the existence of unusual things such as granules or dust particles were carefully observed under various magnifications.

The gravimetric approach was used to determine the specific gravity (*SG*) using a picnometer and an analytical balance. Weighing an empty and oven-dry picnometer (*W1*), a distilled water-filled picnometer (*W2*), and liquefied's adhesive-filled picnometer (*W3*). Equation (1) was used to calculate the specific gravity.

$$SG = \frac{(W3 - W1)}{(W2 - W1} \quad (1)$$

Using ceramic crucibles, a convection oven, and an analytical balance, the solid content (*SC*) was determined using the gravimetric method. The initial sample in the crucible weighed roughly 2 grams (*W1*), and it was then dried in the oven at (103+2)ºC for 24 hours until it reached a constant weight (*W2*). Equation (2) was used to calculate the *SC*.

$$SC = \frac{(W2)}{(W1)} \, x \, 100\% \quad (2)$$

A viscometer with the proper spindle was used to measure viscosity. In a 100 mL beaker glass, a sample of liquefied adhesive was inserted, and measurements were taken at room temperature (27°C) using a spindle with a velocity of rpm (rotary per minute).

The acidity of the liquefied adhesive sample was determined using an electronic pH meter. The sample was placed in a 100 mL beaker glass, and the measurement was taken after the sensitive electrode was saturated in it.

Gel time refers to the time it takes for a liquid adhesive to gelatinize, or change from a liquid to a solid state. In other words, gel time is the amount of time it takes for a liquefied pre-polymer adhesive to solidify or cure. In some circumstances, such as formaldehyde-based adhesives, a hardener or catalyst, such as ammonium chloride (NH_4Cl) for urea-formaldehyde (UF) resin and sodium hydroxide (NaOH) for PF resin, is used to determine gel time. Liquefied adhesive does not require specific conditions such as acidic or alkaline in this study. As a result, a straightforward method for estimating gel time was used. The reaction tube was filled with about 10 grams of liquid glue, which was then placed beneath 2 cm in a boiling water bath. When the sample in the reaction tube hardened, the time calculation was completed.

Free formaldehyde was determined by weighing adhesive sample of 20 g (W). The sample then was mixed with 50 ml distilled water in the Erlenmeyer. Both indicators of methyl red and blue were added 2-3 drops into the mixture and subsequently it was neutralized using either hydrochloric acid (0.1N HCl) or sodium hydroxide (1N NaOH). Afterwards the mixture was added 10 ml of ammonium hydroxide (NH_4OH) 10 wt% and 10 ml NaOH. Erlenmeyer then was covered, shake, and placed in water bath at 30°C for 30 minutes. Titration using HCl was carried out until the colour altered from green into blue-grey and then red-purple (V_1). Using the same procedure, blank solution was made without addition of adhesive sample (V_2). Free formaldehyde (FF) then was calculated using Equation (3).

$$FF = \frac{(V1-V2)x\ 30.03}{(W)}\ x\ 100\% \quad (3)$$

Application for making particleboard

Because the liquefied adhesive has a high viscosity, it requires the addition of a solvent to reduce the viscosity. In this scenario, commercial paint thinner was mixed with liquefied glue in a 1:1 ratio to allow spraying of the particleboard's binder.

Evaluation the quality of resulted particleboard

For particleboard binding, liquefied adhesive with a thinner solvent was used to assess bonding quality. Considering concept of bio-refinery, the particleboard was made from OPT particles (*A*). For comparison, wood particle of jabon (*Anthocephalus cadamba*) as by product of a nearby sawmill was employed because usually particleboard was manufactured using wood particle. Because the wood was categorized as local sawmill waste, it was sieved (30 mesh) and oven-dried (until MC of 5%) before being used to make particleboard. Treatment was consisted of aforementioned *A*, mixture of OPT particle and wood particles with ratio of 50:50 (*B*) and only the wood particle (*C*).

Based on oven dry wood particle, particleboard was developed by combining wood particles with 10% liquid level. The particleboard's target dimensions and density were 25 cm x 25 cm x 1 cm and 0.75 g/cm^3, respectively. For curing the liquid adhesive, a hot press was used at a temperature of 130°C and a pressure of 25 kg/cm^2 for 10 minutes.

Particleboard was made with three replications for each particle, resulting in 9 boards. The finished particleboards were conditioned for 7 days before being cut into specimens in accordance with Japanese Industrial Standard (JIS) A 5908-2003. The density, MC, thickness swelling for 2 and 24 hours, and water absorption for 2 and 24 hours were all assessed using gravimetric techniques. The Tensilon RTF-1350 Universal Testing Machine (UTM) was used to evaluate the mechanical properties of particleboard, including modulus of elasticity (MOE), modulus of rupture (MOR), and internal bonding (IB).

For each parameter, the values of physical and mechanical qualities were tabulated. The data was then statistically analyzed, and Duncan's multiple range tests (DMRT) were used to examine statistical significance at a p value of 0.05 for quantitative measurements of particle type differentiation within the board, namely type particle of OPT (*A*), type particle of mixture of OPT and wood (*B*), and type particle of wood (*C*).

Results and Discussions

Production of liquefied adhesive made of oven dry particles (MC 5%) of vascular bundles of OPT without considering position on the trunk resulted yield 21% with very high viscosity. This value was lower compare to previous work of Esteves et al. [34] who made liquefied adhesive using bark and branches of eucalyptus tree. They have been obtained yield of 62% and 48%, respectively. This was probably because of different solvent used. In converting parts of eucalyptus, mixture of glycerol and ethylene glycol was used as solvent while in this work phenol was used. Indeed, more phenol used, the resulted liquefied adhesives was less viscous as study of Widiyanto et al. [35] who used ratio of P/F = 3. The majority of studies on biomass liquefaction have looked at the effect of the liquefaction solvent on the biomass ratio. According to the findings, the liquefaction solvent served a dual purpose during the liquefaction process, activating reactive sites on biomass components while also terminating reaction intermediates and final products, shifting the reaction to the liquefying direction and preventing re-condensations of decomposed biomass components. To accomplish a proper liquefaction, an excessive amount of liquefaction solvent is necessary. In the case of phenol liquefaction, a significant amount of unreacted phenol was discovered after the reaction [36].

In this study, the type of resulted liquefied adhesive is suitable only for making bond-line by spreading technique such as for plywood making. However, it is impossible for spraying application likewise in particleboard or fibreboard production. The viscosity was too high thus the adhesive could not through-out spray gun' s nozzle. Consequently, addition of solvent after liquefaction synthesis was needed for lowering the viscosity. In this work, commercial thinner was employed for lowering the viscosity of liquefied adhesive since water as polar solvent was not capable to dissolve the liquefied adhesive. Ratio of 1:1 between resulted liquefied adhesive and commercial thinner was applied in order to get proper viscosity. The basic properties of resulted liquified adhesive was summarized in Table 2 as follow:

Table 2. Properties of liquefied adhesive made of OPT

Properties	Result	Criteria of Indonesian Standard (SNI) 06-4567-1998 for PF resin
Color	Brown-blackish	Red-blackish
SG	1.26	1.165-1.200
SC (%)	43	40-45
Viscosity (cP)	96	130-300
pH	7.8	10-13
Gel time (minutes)	98	>30
Free formaldehyde (%)	Not detected	<1

Basic properties of resulted liquefied adhesive

According to Indonesian Standard (SNI) 06-4567-1998 for PF adhesive, the colour should be red-blackish but resulted liquefied adhesive showed brown-blackish. Neither peculiar granule nor dust has not been found in this adhesive. The brown colour indeed originated from lignin content from oil-palm particle. Works of Widiyanto [35] and Risnasari & Ruhendi [37] in making liquefied adhesive made from wood (teak, keruing and agathis) and mixture of rubber wood and bamboo, respectively, resulted in black colour. When Shenyuan et al. [38] liquefied bamboo, brown color was appeared. Lignin content in wood may vary among species of woody plants, some of them could reach 30% [39] but only around 20% within vascular bundles of OPT [33].

Specific gravity (*SG*) of resulted liquefied adhesive was 1.26. This value was little out of range within the standard (1.165-1.200) although previous works on liquefied adhesive exhibited either higher or lower values, for instances 1.23-1.25 [37] and 1.153 [35] depended on the raw materials used. Higher value of *SG* was more than one (>1) means the liquefied adhesive sinks down within water.

SC was percent solid after evaporation of liquid and volatile materials. Liquefied adhesive in this work showed 43% after addition of thinner solvent. This value was in the range of standard with required between 40 and 45%. Prior to mixing with commercial thinner, the *SC* was 86%. Even though it was relatively higher, if comparing with other adhesives such as isocyanate, this value was still lower. Isocyanate has 98-99% solid and indeed it derived from petroleum based [40].

Generally, application of solvent for making liquefied adhesive, so called solvolysis [31,36] has been done in the early stage of liquefaction. Solvent liquefaction is, in fact, the most efficient way to liquefy lignocellulosic materials [41]. In this study, solvent was added both early and late in the process to lessen the viscosity, which was an issue for application processing, particularly for those who used a spray approach. To reduce the viscosity of final products, Kunaver et al. [42] substituted diethylene glycol for glycerol, however in our study, thinner was added to achieve the desired viscosity. Work of Ding et al. [43] involved water in the early stage to control the viscosity. In our case, water could not be added since the liquefied adhesive cannot dissolve in water. The polymeric structural component of OPT will be broken down in the early stages of our technique, and then the liquefaction solvent will react with these broken-up pieces to generate a derivative, which will then all dissolve in the free solvent in the latter stages, resulting in lower viscosity. The final viscosity of the liquefied glue was 96.22 cP, which was similar to our prior study [44] and close to the standard range of 130-300 cP. This viscosity enabled spraying application for producing fiberboard or particleboard.

The acidity of liquefied adhesive tends to alkaline about 7.8. This condition was affected by addition of NaOH at the final stage of liquefaction. This condition was beneficial for surface cleaning (it dissolved the existing contaminant) and for swelling (it enhanced the penetration of adhesive used) [37].

As the gel time increase, the life use of the adhesive is longer. Liquefied adhesive in this experiment required 98 minutes for hardening or curing. This value is in accordance with the standard which required more than 30 minutes. Addition of liquefied adhesive into commercial resin adhesive lengthen the gel time [42, 45].

In this experiment, free formaldehyde was not detected. After HCl titration, there was no colour alter which indicated there was no free formaldehyde within the liquefied adhesive. Lack of emission is most likely owing to a large number of high-reactivity phenolic and alcoholic hydroxyl groups within the liquid adhesive reacting with free formaldehyde [42]. Further, Kunaver et al. [42] also stated that depolymerization products of lignin in liquefaction process participated as radical scavengers which readily react with free formaldehyde due to high reactive characteristics of their aromatic in the mixture during crosslinking process.

Physical properties

Density, MC, thickness swelling, and water absorption were all factors in particleboard's physical qualities. The density of the particleboard produced was shown in Fig.1. The readings met the JIS A 5908-2003 standard, albeit being below the desired density. According this standard, resulted particleboards were classified as medium density particleboard. There was no statistically significant difference between the boards. This means that when raw materials contact with liquefied glue, they all have a similar nature. Droplets of liquid adhesive adhered to the adherents' surfaces. The droplets were then solidified, cured, and bound the adherents with the help of a high temperature from a hot-press. Recent work of Choowang & Luengchavanon [46] indicated that hot pressing with temperature of 160-200ºC enhanced the resulted panels made of OPT.

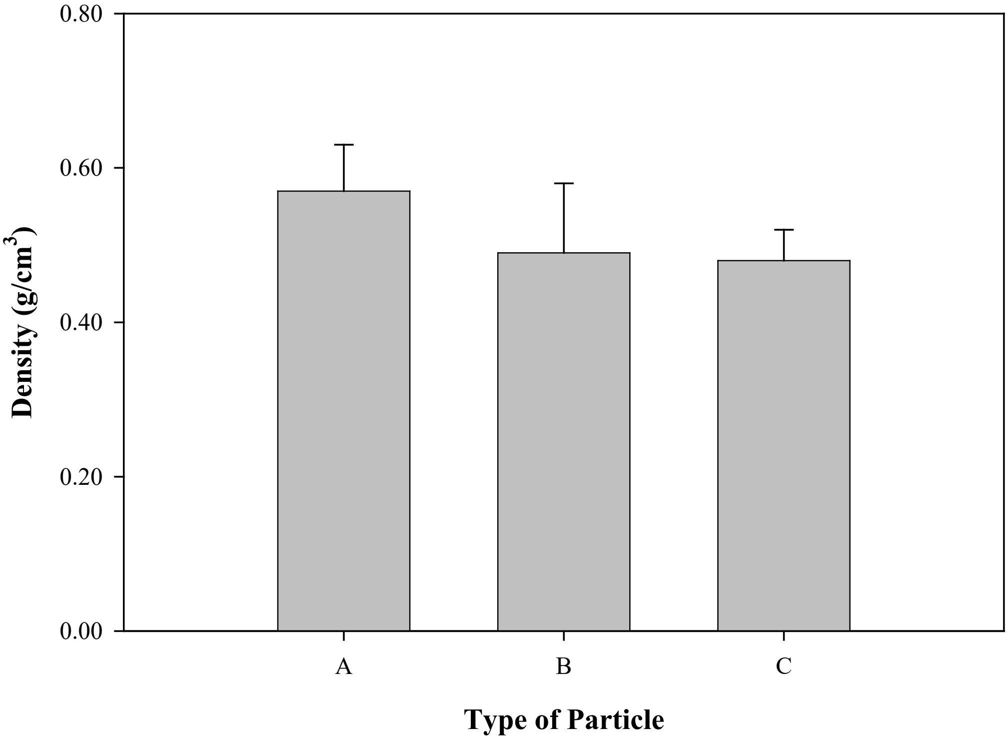

Figure 1. Density of the particleboard

The JIS A 5908-2003 standard required MC of particleboard in the range of 6-12%. Fig. 2 showed MC of the particleboards were around 6-8% which met the criteria of the standard. However, particleboard made of mixture of OPT and wood (B) exhibited lower value and statistically different compared to particleboard with homogenous particle of OPT (A) and particleboard with jabon wood (C). This presumably because of non-homogenous particles arrangement. Further, analysis on lignin of OPT showed of crystalline silica contamination [47] which presumably ruined the compactible between OPT and jabon wood particle.

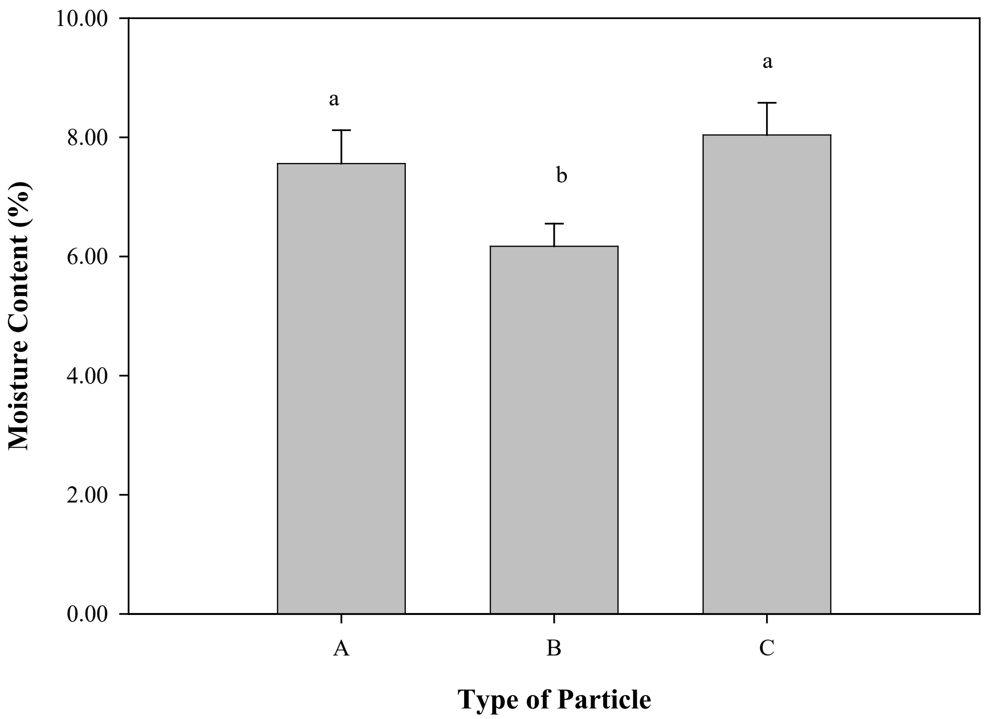

Figure 2. Moisture content of the particleboard

The thickness of the boards increased when they were immersed in water for swelling testing, but there were no statistically significant differences. Furthermore, as shown in Fig. 3, DMRT analysis revealed no significant changes across the tested boards after 2 hours or 24 hours of observation. The values of thickness swelling exceeded the standard limit of JIS A 5908-2003 which required less than 12%. These results were also similar with Kunaver et al. [42] and Ruhendi & Sucipto [48]. These means liquefied adhesive was still less capable to hinder extreme moist condition. In other words, modification of synthesis technology for intensifying the crosslinking reaction have been still needed.

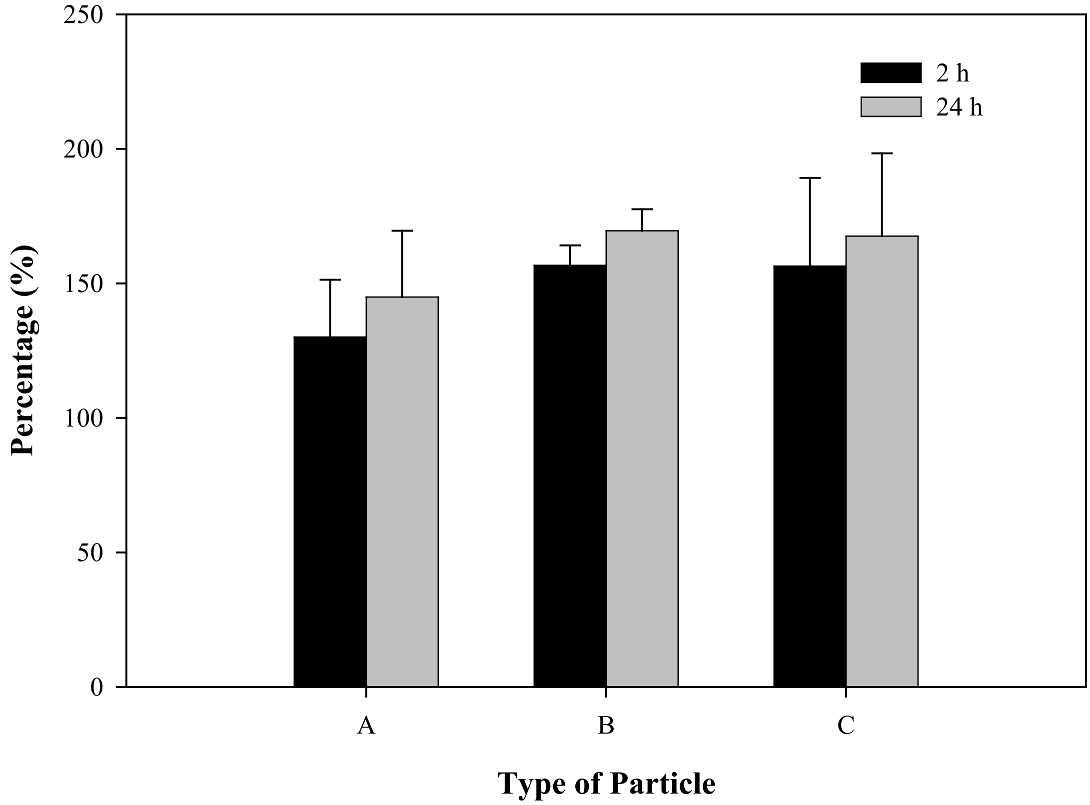

Figure 3. Thickness swelling of the particleboard

Related to thickness swelling of the boards which was caused by soaking in water, Fig. 4 showed percentage of water absorption of the boards which depended on period of time exposed to water. The long duration of the board contact to water, the higher percentage of the water absorption. This trend was comparable to the thickness swelling noted earlier. The DMRT results also revealed that there were no significant differences between the boards when it came to the time of immersion in water, which ranged from 2 to 24 hours. Because the board was made of lignocellulosic materials with hygroscopic properties, this phenomenon was comprehensible. Furthermore, Pan [36] noted that liquefied biomass-based resins have higher water absorption and dimensional instabilities than petroleum-based resins, as well as hydrophilic properties and strong compatibility with lignocellulosic materials.

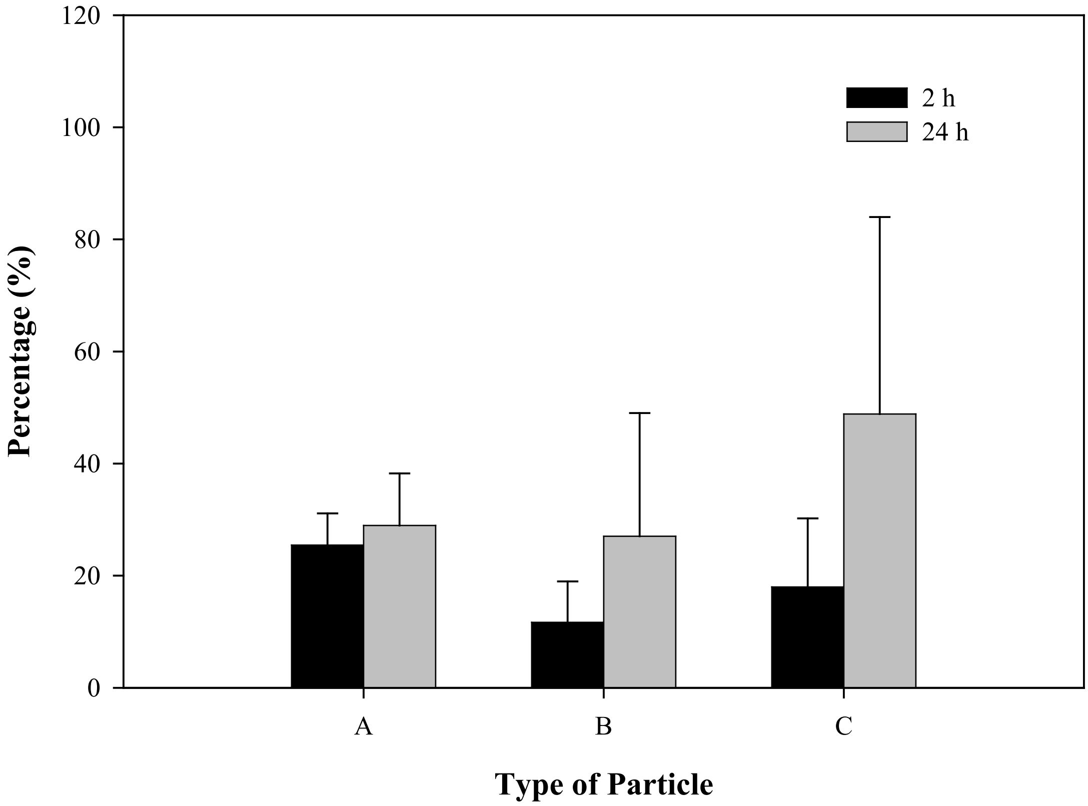

Figure 4. Water absorption of the particleboard

Mechanical properties

Fig. 5 showed the effect of particle used to the MoE and MoR, respectively. MoE fulfilled the standard as the requirement was 20 x 10^3 kgf/cm^2 on the contrary MoR failed because the standard requirement was 80 kgf/cm^2.

In this figure, it is clear from statistical analysis that the MoE was significantly affected by composition type of particle used. When homogenous particles were applied, the MoE values tend to high *vice versa* to that of mixture of particles. OPT and wood naturally were different, the first was monocotyledon and in this study the vascular bundles were considered.

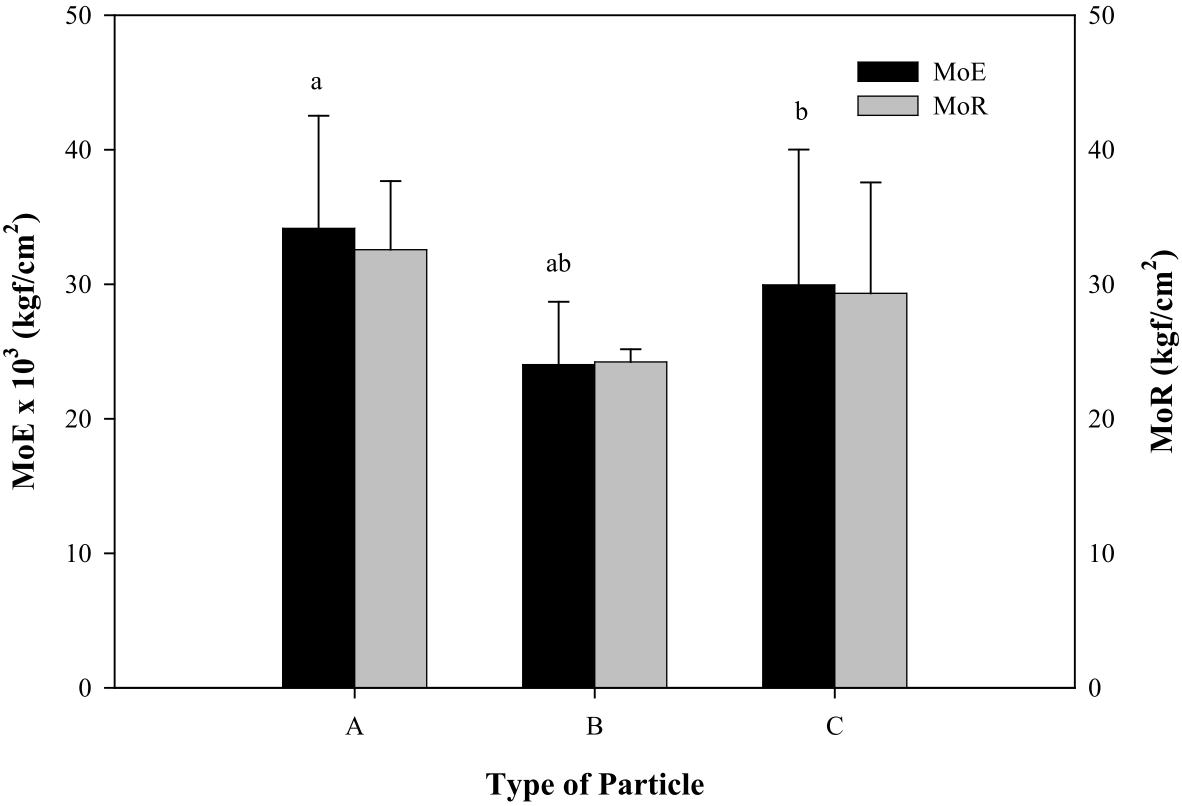

Figure 5. Modulus of elasticity (MoE) and Modulus of rupture (MoR) of the particleboard

Trend of MoR's values were similar to MoE even though statistically not different significantly among the board. However, from the value of the board with type of mixture material (B), it showed the worst strength. This implied that the composition of raw material influenced the quality of the board. In this context, raw material of the board should interact with liquefied adhesive thus compatibility within the board was reached, resulted in not only enhanced strength but also improved internal bonding.

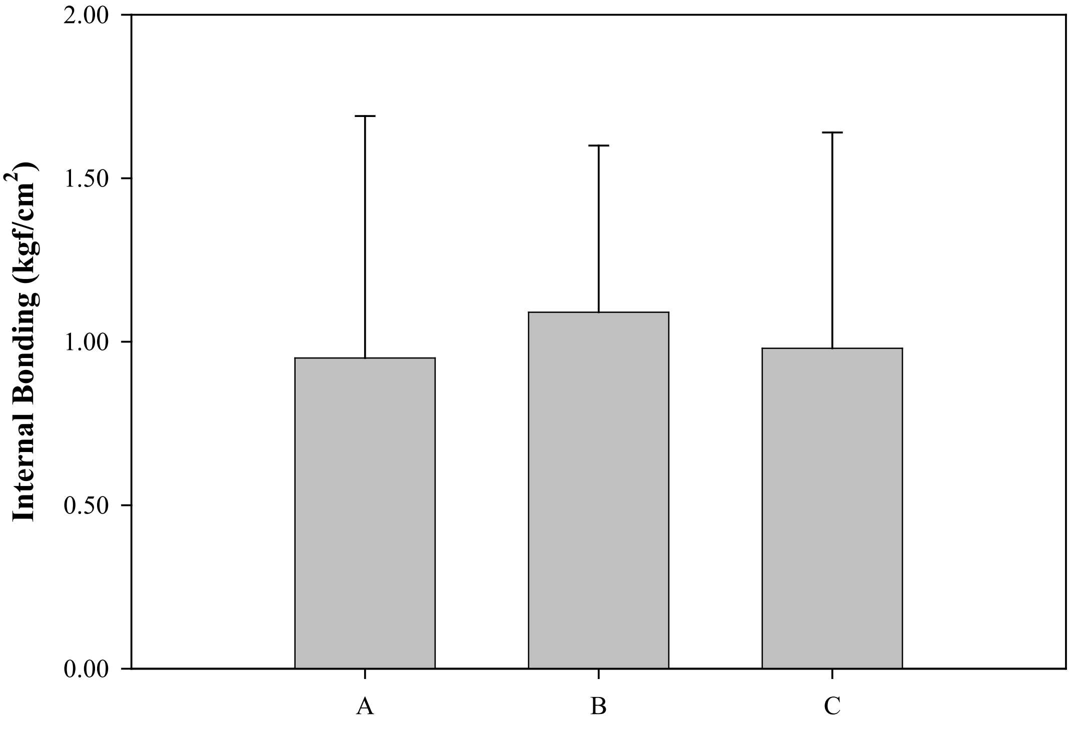

Figure 6. Internal bonding of the particleboard

Unfortunately, in this study, value of internal bonding was lower the standard as shown in Fig. 6. JIS A 5908-2003 required minimum 1.50 kgf/cm^2 but in this study the values were around 1 kgf/cm^2. According to Pan [36], the mechanical strength of liquefied biomass-based resins is often lower due to the reduced reactivity of lignocellulosic derivatives contained in the resin, and hence the resins have lower crosslink density.

Conclusions

Liquefied adhesive made of vascular bundle of oil-palm stem has been successfully synthesized. The properties generally fulfilled the standard excluding the viscosity. This study was the first attempt lowering viscosity after synthesis by mixed with commercial solvent (thinner) for proper spraying for manufacturing particleboard. The resulted boards made of homogenous particles such as OPT particle and jabon wood particle showed better characteristics compared to that of mixture of the two. This finding suggested this liquefied adhesive can be beneficial as a substitution of aldehyde-based adhesive for particleboard industry, since its quality was similar to PF adhesive and formaldehyde emission was not detected. The use of this liquefied adhesive in particleboard industry can expand the potential value of biomass in industrial production and applications in the future.

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References

[1] E. Barcelos, S.A. Rios, R.N.V. Cunha, R. Lopes, S.Y. Motoike, E. Babiychuk, A. Skirycz, S. Kushnir, Oil palm natural diversity and the potential for yield improvement, Frontiers in Plant Science 6 (2015) 190.

[2] N.A.M. Hassim, N.L.H.M. Dian, Usage of palm oil, palm kernel oil and their fractions as confectionery fats, Journal of Oil Palm Research 29 (3) (2017) 301-310.

[3] W.R.A. Isa, N.A. Idris. Physico-chemical characteristics of palm-based oil blends for ice cream, Palm Oil Developments 46 (2020) 8-14.

[4] Z.A.Z. Hasan, Z. Idris, R. Ismail, H.A. Hassan, Safety and efficacy of palm-based ingredients in cosmetic and personal care products, Oil Palm Bulletin 62 (2011) 33-42.

[5] K. C. Yong, T. L Ooi, K. Dzulkefly, W.M.Z.W. Yunus, A.H. Hazimah, Characterization of glycerol residue from a palm kernel oil methyl ester plant, Journal of Oil Palm Research 13(2) (2001) 1-6.

[6] A. Rabiu, S. Elias, O. Oyekola, Oleochemicals from palm oil for the petroleum industry in: Palm oil, Intechopen, Croatia, 2018, pp. 91-115.

[7] K.A. Zahan, M. Kano, Biodiesel production from palm oil, its by-products, and mill effluent: a review, Energies 11 (2018) 2132.

[8] I. Singh, R.S. Nair, S. Gan, V. Cheong, A. Morris, An evaluation of crude palm oil (CPO) and tocotrienol rich fraction (TRF) of palm oil as percutaneous permeation enhancers using full-thickness human skin, Pharmaceutical Development and Technology 24(4) (2019) 448-454.

[9] O. Sulaiman, N. Salim, N.A. Nordin, R. Hashim, M. Ibrahim, M. Sato, The potential of oil palm trunk biomass as an alternative source for compressed wood, Bioresources 7(2) (2012) 2688-2706. Doi: 10.15376/biores.7.2.2688-2706.

[10] H.P.S.A. Khalil, M. Jawaid, A. Hassan, M.T. Paridah, A. Zaidon, Chapter 8. Oil Palm Biomass Fibres and Recent Advancement in Oil Palm Biomass Fibres Based Hybrid Biocomposites in: Composites and Their Applications, http://dx.doi.org/10.5772/48235, 2012.

[11] R. Dungani, M. Jawaid, H.P.S.A. Khalil, Jasni, S. Aprilia, K.R. Hakeem, S. Hartati, M.N. Islam, A review on quality enhancement of oil palm trunk waste by resin impregnation: future materials, BioResources 8(2) (2013).

[12] S.N. Shafawati, S. Siddiquee, Composting of oil palm fibres and *Trichoderma* spp. as the biological control agent: a review, International Biodeterioration & Biodegradation 85 (2013) 243-253.

[13] [FAO] Food and Agriculture Organization. Forestry Production and Trade, Available online: http://www.fao.org/faostat/en/#data/FO, accessed on Dec 25, 2020.

[14] N.A. Samiran, M. Jaafar, M. Nazri, C.T. Chong, J.H. Ng, A review of palm oil biomass as a feedstock for syngas fuel technology, Jurnal Teknologi 72 (5) (2015) 13-18.

[15] S. Mohamed, Oil palm leaf: a new functional food ingredient for health and disease prevention, Journal of Food Processing & Technology, 5(2) (2004) 1-6.

[16] M.W. Zahari, O.A. Hassan, H.K. Wong, J.B. Liang, Utilization of oil palm frond - based diets for beef and dairy production in Malaysia, Asian-Aust. J. Anim. Sci., 16(4) (2003) 625-634.

[17] A. Lim, J.J. Chew, L.H. Ngu, S. Ismadji, D.S. Khaerudini, J. Sunarso, Synthesis, characterization, adsorption isotherm, and kinetic study of oil palm trunk-derived activated carbon for tannin removal from aqueous solution, ACS Omega 5 (2020) 28673-28683.

[18] K. Hassan, J. Kasim, A. Mokhtar, A. A. Aziz, Characterisation of oil palm trunks and their holocellulose fibres for the manufacture of industrial commodities, Oil Palm Bulletin 63 (2011) 11-23.

[19] J.P. Tan, J.M. Jahim, S. Harun, T.Y. Wu, T. Mumtaz, Utilization of oil palm fronds as a sustainable carbon source in biorefineries, International Journal of Hydrogen Energy 41 (2016) 4896-4906.

[20] K. Nordin, M.A. Jamaludin, M. Ahmad, H.W. Samsi, A.H. Salleh, Z. Jalaludin, Management of Environmental Quality: An International Journal 15(5) (2004) 484-490.

[21] R. Wahab, M.A. Salam, O. Sulaiman, M. Sudin, H.W. Samsi, M.S.M. Rasat, Properties of engineered oil palm composite boards from 32 year-old tree stems, ARPN Journal of Agricultural and Biological Science 8(7) (2013) 541-545.

[22] F. Rosli, C.M.R. Ghazali, M.M.A.B. Abdullah, K. Hussin, A review: characteristics of oil-palm trunk (OPT) and quality improvement of palm trunk plywood by resin impregnation, BioResources 11(2) (2016) 5565-5580.

[23] S.C. Lim, K.S. Gan, Characteristics and utilization of oil-palm stem, Timber Technology Bulletin 35 (2005) Forest Research Institute Malaysia.

[24] S.F.M. Ramle, O. Sulaiman, R. Hashim, T. Arai, A. Kosugi, H. Abe, Y. Murata, Y. Mori, Parenchyma and vascular of oil-palm, Lignocellulose 1(1) (2012) 33-44.

[25] H. Mansor, A.R. Ahmad, Carbohydrates in the oil-palm stem and their potential use, Journal of Tropical Forest Science 2(3) (1990) 220-226.

[26] R. Dirkes, P.R. Neubauer, J. Rabenhorst, Pressed sap from oil palm (*Elaeis guineensis*) trunks: a revolutionary growth medium for the biotechnological industry? Biofuels, Bioprod. Bioref. 15 (2021) 931-944.

[27] K.M. Salleh, R. Hashim, O. Sulaiman, S. Hiziroglu, W.N.A.W. Nadhari, N.A. Karim, N. Jumhuri, L.Z.P.Ang, Evaluation of properties of starch-based adhesives and particleboard manufactured from them, Journal of Adhesion Science and Technology 29(4) (2015) 319-336.

[28] M.J. Lubis, I. Risnasari, A. Nuryawan, F. Febrianto, The quality of composite board made of waste oil-palm stem (*Elaeis guineensis* Jacq.) and recycle polyethylene (PE), J.Agroindustrial Technology 19(1) (2009) 16-20.

[29] A. Nuryawan, Manufacturing of oriented strand board made of vascular bundles of oil-palm stem, Indonesian Patent pending P00201000838 (2010).

[30] A. Ugovšek, F. Budija, M. Kariž, M. Šernek, The influence of solvent content in liquefied wood and of the addition of condensed tannin on bonding quality, Drvna Industrija 62(2) (2011) 87-95.

[31] W. Jiang, A. Kumar, S. Adamopoulos, Liquefaction of lignocellulosic materials and applications in wood adhesives-A review, Industrial Crops & Products 124 (2018) 325-342.

[32] T.L. Chew, S. Bhatia, Catalytic processes towards the production of biofuels in a palm oil and oil-palm biomass-based biorefinery, Journal of Bioresource Technology, doi:10.1016/j.biortech.2008.03.009 (2008).

[33] A. Nuryawan, A. Dalimunthe, R.N. Saragih, Physical and chemical properties of oil palm trunk vascular bundles, FORESTA, Indonesian Journal of Forestry 1 (2) (2012) 34-40.

[34] B.M.D.M.L. Esteves, L.P.V. Cruz-Lopez, A.P. Fernandes, J.M. Martins, I.D.J. Domingos, J.V. Ferreira, S.H.F.D. Silva, J. Labidi, Adhesives from liquefied eucalypt bark and branches, Wood Research 64(1) (2019) 105-116.

[35] A. Widiyanto, Quality of particleboard of rubber wood (*Hevea brasiliensis* Muell. Arg) and tali bamboo (*Gigantochloa apus* Kurz) with wood liquids adhesive, Journal of Forest Products Research 29(4) (2011) 301-311.

[36] H. Pan, Synthesis of polymers from organic solvent liquefied biomass: A review, Renewable and Sustainable Energy Reviews 15 (2011) 3454-3463.

[37] I. Risnasari, S. Ruhendi, Characteristics of wood liquid adhesives from several wood species, Peronema Forestry Science Journal 2(2) (2006) 66-70.

[38] F. Shenyuan, M. Lingfei, L. Wenzhu, C. Shuna, Liquefaction of bamboo, preparation of liquefied bamboo adhesives, and properties of the adhesives, Front. For. China 2 (2011) 219-224.

[39] M.M. Campbell, R.R. Sederoff, Variation in lignin content and composition, Plant Physiology 110 (1996) 3-13.

[40] A. Nuryawan, E.M. Alamsyah, Thermal properties of isocyanate as particleboard's adhesive, IOP Conf. Series: Materials Science and Engineering 593 (2019) 012004.

[41] W.J. Lee, M.S. Lin, Preparation and application of polyurethane adhesives made from polyhydric alcohol liquefied Taiwan acacia and China fir, Journal of Applied Polymer Science 109 (2008) 23-31.

[42] M. Kunaver, S. Medved, N. Čuk, E. Jasiukaitytė, I. Poljanšek, T. Strnad, Application of liquefied wood as a new particle board adhesive system, Bioresources Technology 101 (2010) 1361-1368.

[43] F. Ding, Y. Qiu, Z. Liu, Q. Zhang, Optimization of resinification of liquefied products from trash ACQ-treated antiseptic wood, Advanced Materials Research 479-481 (2012) 31-35.

[44] A. Nuryawan, I. Risnasari, D. Situmorang, Application of liquefied adhesive made of oil-palm stem for particleboard binder, IOP Conf. Series: Earth and Environmental Science 454 (2020) 012088.

[45] B. Esteves, J. Martins, J. Martins, L. Cruz-Lopes, J. Vicente, I. Domingos, Liquefied wood as a partial substitute of melamine-urea-formaldehyde and urea-formaldehyde, Maderas. Ciencia y tecnología 17(2) (2015) 277-284.

[46] R. Choowang, M. Luengchavanon, Oil palm trunk powder blended with citric acid directly used as wood adhesive by one step liquefaction reaction, Industrial Crops & Products 170 (2021) 113809.

[47] Y. Tomimura, Chemical characteristics of oil palm trunk, Bull. For. & For. Prod. Res. Inst. 362 (1992) 133-142.

[48] S. Ruhendi, T. Sucipto, Development of wood liquid and particleboard from oil palm empty fruit bunches, Jurnal Ilmu Pertanian Indonesia (JIPI) 18 (2) (2013) 115-124.

CHAPTER 2:

Materials and Technologies for Environmental Engineering and Waste Processing Applications

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Co-Composting Date Palm Tree Wastes and its Effects on Soil Fertility

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Abstract. UAE is one of the world major producer of dates. In 2015, the country had more than 42 million date palm trees and this number is increasing gradually. Every year there is more than 600,000 tons of date palm tree wastes are generated in farms. Since composting of date palm tree wastes is hard and slow, but when mixed with chicken manures it has been improved and time needed for maturation is greatly reduced, and the produced compost has better quality. Amended sandy soil with produced compost showed better physical, chemical and biological properties against control treatment (farm yard manure, FYM). In this experiment we used several treatments e.g chicken manure compost, CMC, and date palm tree composted wastes, DPTCW in different ratios, to evaluate its quality as organic fertilizer and to study its effects on the properties of sandy soils against control, FYM. CMC reached maturation faster than DPTCW and has higher contents of NPK nutrients than DPTWC, while organic matter and humus were different as composting activity performed. Tested sandy soil showed higher organic carbon content and its numbers of microorganisms has been increased in all treatments against control. Date fruits yield was increased in all treatments above control by 27- 62% above control.

Introduction

In the Arabian Peninsula, North Africa and the Middle East date palm (Phoenix dactylifera) is one of the world's oldest trees, grown widely in hot, dry, desert regions,. Date palm tree plays a major role in the life of people in Arabic nations. Date fruits are a key element in food security; therefore scientists' pays attention to the care of date palm trees. Date palm tree is of great socio-economic importance in the Arabian Peninsula countries like United Arab Emirates (UAE), Saudi Arabia, and Oman. The date fruit is one of the most important sources of nutrition for people in the Arabian Peninsula, North Africa and the Middle East.

Date Palm (Phoenix dactylifera L) is considered the most economic crop in agriculture sector in UAE and it has a high energy value crop, with a good nutritional value. It is a long lived monocotyledon cultivated for food, fuel, shelter and fiber. There are more than 105 million date palm trees. United Arab Emirates, UAE is considered as one of the world major producer of dates. Date palm trees produce large quantity of crop residues in UAE, annually totals of 600,000 tons of green wastes, e.g. , each tree produces about 15-25 kg of dry leaves [1,2]. Although the whole palm trees waste consist of hardly decomposed compounds, they could be co-composted with chicken or cow manure instead of burning in farms and causing serious threat to environment.

To meet the increasing demand for food, due to the world population continues to increase at an alarming rate, intensive cultivation using more cropland areas and increased use of fertilizers had been practiced. Chemical fertilizers are the solitarily most important contributor to the rise in the world's agricultural production according to the FAO publications [3]. Fertilizers comprising of N.P.K are regarded as the drivers of modern agriculture. Their worldwide use had been increased since the green revolution. Chemical fertilizers recently provided 317.4 million tons as input to the agricultural soils in which 176.1 million tons was nitrogen, 62.2 million tons was phosphorus (expressed as P_2O_5), and 73.7 million tons was potassium (expressed as K_2O). Fertilizer use increased by about 70% per hectare from 1939 to 2018, which was about 95 tons per hectare. By nutrient, the increase was about 56% for nitrogen, 19.8% for P_2O_5, and 23.44% for K_2O. Low

fertilizer use efficiencies in most of the soils are another factor adding in more use of chemical fertilizers. Also, intensive land use of higher doses of chemical fertilizers significantly influences soil health and crop growth. Soil health is collectively defined by physical (texture, bulk density, infiltration rate, hydraulic conductivity, porosity, etc.), chemical (essential nutrients, cation exchange capacity, electrical conductivity, etc.), and biological (microbial community including bacteria, fungi, algae, protozoa, earthworm, etc.), [3].
Global chemical fertilizers usage trend (1939-2018), showed a massive increase of inorganic fertilizers use in our agriculture sections. Using chemical fertilizers are very important for food security and plant growth, but the misuse of such chemicals can create environmental and economic losses in farms. All farms are producing crop residues and green wastes and these can be recycled and used as organic fertilizer and soil conditioner input and can be a great solution to reduce chemical fertilizer usage and positively reflect income for farmers and improving plant yield and soil properties [3].
The aerobic natural process of decomposing and converting organic wastes into a stabilized form is called composting and the organic produced fertilizer is known as compost (the resulting stabilized organic matter). Co composting cellulosic materials with other farm wastes rich in nitrogen and phosphorus is very important to reduce the C:N:P ratios and to enhance the texture and composting process because usually, agricultural wastes or crop residues contain moderate to high level of moisture content and a wide C/N ratio. Using fish wastes, chicken manure or cow manure are recommended as rich sources of nitrogen and phosphorus, [4,5,6].

Table 1, The trend of global chemical fertilizers usage (1939-2018).

YEAR	**World populations in billions**	**Total fertilizers use (TON 10^6)**	**N (TON 10^6)**	**P_2O_5 (TON 10^6)**	**K_2O (TON 10^6)**
1939	2.0	9.0	5.109	1.781	2.109
1970	3.7	>60.0	34.062	11.874	14.064
1980	4.4	>162.5	92.251	32.158	38.090
1990	5.3	>180.0	102.186	35.622	42.192
2000	6.1	220.0	124.94	43.538	51.568
2008	6.8	250.0	141.925	49.475	58.600
2010	6.9	255.0	144.814	50.464	59.772
2013	7.2	270.0	153.279	53.433	63.288
2018	7.63	317.474	176.103	62.234	73.71

Source: FAO stat publications, 2018.

1. Farm wastes:

A- Date palm tree byproducts and farm wastes:

Date palm residues represent a major quantity of biomass as lignocellulosic materials [7]. This type of recalcitrant biomass, is mostly made up of carbohydrates including cellulose and hemicellulose, bonded with lignin [8]. The lignocellulose content in palm biomass varies from species to another. A review study on Elaeis Guineensis, commonly cultivated in south East Asia, Central and West Africa, showed various results of different palm tree parts and their lignocellulose content [9]. Most of the waste from palm trees is currently turned into compost or burned to generate heat despite their high content of cellulose, hemicelluloses and lignin that can be processed into more valuable products such as fuel generation, bio-based chemical production and all these through controlled thermochemical techniques would cause less environmental impact. For instance for palm fibers, a hemicellulose- 17.1–33.5 wt.%, cellulose- 42.7–65 wt. % and lignin- 13.2–25.31 % content was reported (Shinoj et al, 2011), while another study on Phoenix dactylifera L. species showed hemicellulose- 55 wt.%, cellulose- 20 wt.% and lignin- 23 wt.% content [7,8,9,10].

Crop residues and woody byproducts always have relatively normal to high water content and a wide range of Carbon/Nitrogen ratio. Sawdust and wood shavings are low in Nitrogen and Phosphorus and therefore are composted best if mixed with other counter-balancing materials, or with N and P fertilizers. Wood shavings and wood byproducts contain hemicelluloses and celluloses that break down easily, and the recalcitrant lignin that contribute mainly to humus formation, [11,12].

B- Poultry manure

Global population growth and demand for meat and eggs caused livestock production markedly increased with increasing demand. To take an instance from the global demand for pig meat, chicken meat and chicken eggs, it was predicted to grow by 32%, 61%, and 39%, respectively, up to 2030, [13]. Chicken/poultry droppings is a farm waste material with a high moisture content of up to 45 percent, high nitrogen content and therefore, requires a high carbon make up. Poultry manure with crop residues and/or sawdust or woody shavings is an example of a good material mix for composting. The problem with poultry manure is its high nitrogen content, which during composting may create nitrogen loss and release bad and offensive odor from ammonia. In this case, a proper mix of organic materials must be formulated to ensure the proper amount of oxygen and water levels. Preliminary composting still requires another 4- to 6-week curing stage to produce a mature end product, otherwise can be highly odorous and potentially cause damage to crops and plants, [13,14].

2. Some Factors Affecting Composting Process and End Product Quality

In composting there are several and most important factors controlling the composting process, e.g. pH, temperature, Particle size, Porosity, texture, moisture content and C/N ratio [14,15,16]. The optimum target pH level is between 6.0 and 8.0. The pH values fluctuate depending on the type of raw materials used in the compost mix and the production of different products during composting. Subsequently, the pH value always drops to a range of acidic level, e.g. 4 to 5 due to generation of organic fatty acids and usually during the stability or maturation period it reaches the neutral level of pH 7.0 and this stage can be short or medium or long relatively with the simplicity or complexity of chemical composition of composting materials, since simple compound reach maturation much faster than complex mixes. Also, temperature, during composting is considered as one of the key factors that indicates microbial activity in the compost pile. Composting is a multi-phased process, with varying temperature ranges in each phase, defined by the types of micro-organisms that dominate the pile during rising temperatures. As the temperature varies, it affects the rate of reactions and thus conditions become inappropriate for some micro-organisms while at the same time becoming suitable for others. While, Particle size is also closely related to the porosity, texture and structure of the waste material. They stated that, Since decomposition level during composting is affected by the particle size of the composting raw materials and the decomposition occurs primarily on or near the surfaces of particles. Smaller particles have greater surface area per unit mass or volume than large particles, so if aeration is adequate small particles will degrade more quickly. The ideal particle size, within the range of 10 to 50 mm, has enough surface area for rapid microbial activity but also adequate spaces to allow air to circulate for microbial activity [14,15,16]. Porosity, is a measure of the pore sizes (air) space of a material or pile of materials within the compost mix. These spaces between the particles that create the structure affect the resistance of airflow through the pile. Texture is the available surface area of particles. A fine texture implies many small particles with a large combined surface area. A course texture implies large particles with less overall surface area. While, structure is the ability of particles to resist settling and compaction, and it is important in establishing and maintaining porosity during the composting process. To reach and have optimum particle size of compost material must be a balance between maximizing porosity, surface area and increasing structure. For having high microbial activity, it is advisable to maintain the moisture level near 50-60 % during the composting active phases, then gradually moisture drop toward maturation.

When combining organic materials to make compost, the C/N ratio is important as both elements are very important for the composting. Always microbes need a source of energy and a source of nitrogen which is derived from carbon and another source of protein that is derived from nitrogen elements, which is called carbon to nitrogen (C/N) ratio, where the Carbon serves as an energy source much of which is released as carbon dioxide and heat, and the Nitrogen provides additional nutrition and protein synthesis to continue growing and reproducing. Therefore, the ratio carbon (C) to nitrogen (N) in an organic material is a key factor in composting process. A C/N ratio within the range of 25 to 40:1 results in an successful process while a C/N ratio of 30 is optimal was reported by [14,15,16]. Inadequate nitrogen (a high C/N ratio) results in limited microbial biomass and slow feedstock decomposition and poor compost end product regarding to its nutrients availability to plants. Excess nitrogen (a low C/N ratio) is likely to produce a loss of ammonia gas or nitrate, as usually happened in composting chicken manure or fish wastes alone [17].

3. Compost end product maturity

Composting process can be a period of 3 to 4 months until compost becomes stable at a near–ambient temperature level and an acceptable oxygen content. Mature and finished compost must have earthy odor, black or brown color and free from pathogens and weed seed. And meet the regulation set by country authorities, e.g. municipalities and ministry of agriculture regulation for handling and selling compost and soil conditioners.

In this experiment we needed to study the possibility of producing organic compost with high quality using date palm trimming and chicken manures to produce the compost which will contribute to reducing the usage of inorganic chemical fertilizers and enhancing the environment, and creating extra income for farmers by adopting the circular economy when recycling the farm wastes and producing high quality compost.

Materials and Methods:

To study the effect of mixing chicken manure as enhancement process for composting date palm wastes, this experiment was conducted in the year 2019 at al-Ain UAE, and to study the effect of composting different farm wastes e.g chicken manure, date palm tree leaves and its different mixtures on compost quality and its effects on some soil properties. Date palm leaves and chicken manures were collected, and date palm tree leaves were chopped to half inch pieces. Four different compost piles were prepared of 10 tons each. Materials were tested for its moisture, organic matter content and nitrogen contents. Composted materials were subject to turning weekly for a period of 120 days. Periodical samples were taken for testing the compost performance. The end product was studied for its effect on sandy soil properties e.g. physical, chemical and biological properties when adding 25 kg per tree, against the traditional organic fertilizer (farm yard manure as experiment control treatment. Date fruit yield was also evaluated.

Soil content of organic matter was 0.21, pH value was 8.3 total phosphorus was 0.39% and calcium carbonate was 18.0 %. 25 date palm trees of (Neghal variety of seven years old and identical trees) were selected and divided into five groups, and each treatment of five replicates, and the treatments were as follow:

1- Control is normal farm yard manure (FYM).

2- Chicken manure 100%, (CM).

3- Date palm tree leaves 100%, (DPTL).

4- Mixed date palm tree leaves, (75%) + 25 % chicken manure compost.

5- Mixed date palm tree leaves, (50%) + 50 % chicken manure compost.

Methods:

Compost sampling and analysis: Compost piles were turned and thoroughly mixed weekly. After mixing, compost samples were collected using sampling core (at the periodical interval up to 120 days). Fresh compost samples were dried at 65 °C for approximately 48 hrs. then, ground and sieved with 2 mm sieve for chemical analysis. The total C and N contents were analyzed by an elemental analyzer, ammonia and nitrate nitrogen by titration after steam distillation. pH and EC measured in 1:5 water ratio using Jinway apparatus. . Chemical analysis followed [18,19,20].

Soil and compost analysis: 25 kg of produced compost / organic fertilizers materials were mixed thoroughly around the tree in the 15-20 cm depth and irrigated immediately. Soil samples were taken periodically for testing. Soil samples were taken at the intervals of, 7, 30, 60, 90, 120, and 180 days for testing soil properties. At the harvest time, also, the yield of fruits also measured.

To study the effect of treatments on soil microbial activity and organic matter content. All biological analysis followed the slandered methods after, APHA. [21] and media was prepared according to Diffco manual [22].

Table 2, Initial analysis, of materials used in the study.

Parameter	Farm yard manure (FYM)	Date palm tree leaves (DPT)	Chicken manure (CM)	DPT + 25% CM	DPT + 50% CM
Moisture (%)	22.0	27.1	45.0	36.2	42.0
Organic matter (%)	23.0	92.4	74.2	78.2	81.6
Total nitrogen (%)	0.57	0.61	2.4	1.8	1.62
Organic carbon (%)	13.37	53.59	43.1	45.35	47.33
C/N Ratio	23.4	87.8	8.9	25.2	29.2

Results & Discussions:

1. Evaluation of composting process:

The composting process, its maturation and nutrients content e.g. Organic matter (%),Total nitrogen (%). Ammonia (ppm), Nitrate (ppm), C/N Ratio, Humus content (%), pH value, and EC for a period of 120 days are presented in Tables (3&4&5&6) which summaries the periodical changes of Some parameters basically affecting the success of the composting process. pH values during composting is an indicator for state of composing, pH values in all treatments showed a similar trend with little changes. Increasing trend in the thermophilic phase were found. That trend could be attributed to the degradation of acid compounds and the increase of ammonia gas. Organic matter decreased towards the end of composting course, and materials behaved differently according the the simplicity or complexity of the composting blend. There was a build up of humus at the end of composting process . The nitrogen is firstly converted into NH4+-N and easily volatilized as NH_3 gas in the thermophilic stage and create bad odors, due to the high temperature and slightly alkaline condition resulted from the decomposition of compost. The NH_4+-N is converted into NO_3−N through aerobic nitrification and anaerobic de-nitrification, during which the N_2O and N_2 gases are produced. The NO_3−-N concentration was low at the initial stage of the composting and increased sharply in the second mesophilic /maturation phase, which is good for improving the quality of organic fertilizer produced, which will be ready available for plant uptake.

Nitrogen content has been reduced as organic mass is reduced and the nitrogen percentage showed increase at the end of composting. This increase in nitrogen content is mainly due to the loss of organic carbon during composting process and the narrowing of the C/N ratio at the maturation stage. C/N ratio is main indicator to present the stability of composting and the maturity of final product. Similar with previous studies, [12,14]. C/N ratio slightly increased at thermophilic stage, it might be due to the N loss caused by ammonia volatilization. The final C/N ratio values of four treatments were less than 25, which is indicated the maturity of the produced compost, except for date palm leaves alone, which require longer period to reach maturation due to its initial composition and high level of lignin in date palm materials. Since the ratio carbon (C) to nitrogen (N) in an organic material is a key factor in composting process as both elements are very important for the composting. A C/N ratio within the range of 25 to 40:1 results in an successful process while a C/N ratio of 30 is optimal [14,15,16]. This was clear result when we do composting date palm leaves alone the process was slow and needed longer time for maturation, while when we mixed chicken manure with date palm leaves, there was a speed up of composting process and end the product was higher in quality. These results are in full agreement with, [23,24,25]. It was clear that, insufficient nitrogen (a wide C/N ratio) results in poor and less quantity of microbial biomass and slow feedstock decomposition. While, excess nitrogen in chicken manure alone treatment (a low C/N ratio) is likely to produce a loss of ammonia gas or nitrate. Humus content increased in all treatments toward maturation. Treatment of mixed chicken manure showed higher contents of humus than chicken manure alone while composted date palm tree leaves came at last with lower humification process due to the slow rate of composting. Mixing chicken manure with date palm leaves enhanced the process due to its quality and content of needed nutrients and high microbial counts, [23,24,25].

Table 3, Changes of some parameters during composting of chicken manure wastes.

Parameter	Time (days)						
	0	7	14	30	60	90	120
Organic matter(%)	74.2	71.5	68.9	66.0	61.0	57.6	51.9
Total nitrogen (%)	2.4	2.4	2.6	2.7	2.9	3.1	3.2
Ammonia (ppm)	0.9	2.2	6.9	9.7	4.4	1.6	1.4
Nitrate (ppm)	0.1	0.3	0.9	1.3	1.6	1.9	2.4
C/N Ratio	17.9	17.2	15.3	14.1	12.2	10.8	9.4
Humus content (%)	4.7	5.2	8.1	11.3	15.8	18.0	20.1
pH value	7.8	6.9	8.6	8.8	8.4	8.1	7.2
EC (dS/m)	12.0	13.1	15.2	16.0	14.7	13.6	12.0

Table 4, Changes of some parameters during composting of 25.0 % chicken manure wastes mixed with 75% DPT leaf wastes.

Parameter	Time (days)						
	0	7	14	30	60	90	120
Organic matter(%)	78.2	77.1	76.0	74.0	72.6	70.6	69.2
Total nitrogen (%)	1.80	1.66	1.7	1.72	1.73	1.75	1.77
Ammonia (ppm)	0.8	1.1	1.9	4.7	3.4	1.6	1.4
Nitrate (ppm)	0.2	0.3	0.9	1.6	1.8	2.1	2.4
C/N Ratio	25.1	26.9	25.6	24.9	24.3	23.1	22.6
Humus content (%)	4.5	6.2	8.0	11.8	16.8	17.0	21.4
pH value	7.8	6.9	8.3	8.2	8.0	7.8	7.2
EC (dS/m)	13.0	13.1	14.2	15.0	14.0	13.6	11.0

Table 5, Changes of some parameters during composting of 50.0 % chicken manure wastes mixed with 50% DPT leaf wastes.

Parameter	Time (days)						
	0	7	14	30	60	90	120
Organic matter(%)	81.6	80.8	76.0	72.0	69.2	67.0	65.2
Total nitrogen (%)	1.62	1.55	1.63	1.68	1.74	1.77	1.82
Ammonia (ppm)	0.6	1.95	3.30	5.9	4.6	2.6	2.2
Nitrate (ppm)	0.3	0.4	1.0	2.1	2.6	2.9	2.8
C/N Ratio	29.2	30.2	27.0	24.8	22.6	21.9	20.7
Humus content (%)	6.1	7.3	8.6	13.0	15.8	21.4	23.2
pH value	8.3	6.6	8.8	8.2	7.8	7.6	7.2
EC (dS/m)	15.0	15.2	14.8	13.6	13.2	13.0	12.0

Table 6, Changes of some parameters during composting of 100% DPT leaf wastes.

Parameter	Time (days)						
	0	7	14	30	60	90	120
Organic matter(%)	92.4	91.0	89.1	87.2	85.0	81.9	80.1
Total nitrogen (%)	0.61	0.63	0.64	0.66	0.65	0.67	0.69
Ammonia (ppm)	0.7	0.9	1.2	0.7	0.4	0.3	0.2
Nitrate (ppm)	0.1	0.2	0.2	0.3	0.2	0.4	0.4
C/N Ratio	87.8	83.7	80.7	76.6	75.8	70.9	67.3
Humus content (%)	3.1	4.9	6.7	9.2	9.7	10.2	10.5
pH value	8.5	7.4	6.8	5.9	6.3	6.8	7.2
EC (dS/m)	9.3	9.5	9.8	10.8	12	12.1	12

2. Effect of different composts on soil fertility and date palm yield in sandy soils:

Basis for the calculation of the amount of fertilizers required by an adult date palm nutrients lost through fruits and pruned leaves for date palm trees, as well as the world-wide application of fertilizers were considered. Our study was based on related literature, experiments and finding in various countries (Algeria, Iraq, Morocco and USA) [26]. It is estimated that in order to produce 50 kg of date fruits per palm, the fertilization needs are abut 45kg of nitrogen, 13.5kg of phosphate and 81kg of potassium, of which most of it could be covered by irrigation water [26]. In our experiment adding 25 kg of organic compost per tree was studied for its effect on soil properties and date fruit yield of 7 years old Neghal date palm trees.

Table (7) Depicted the composted materials end products quality. It is very clear from the results that composted chicken manure showed the fastest rate of composting, and higher amounts of carbon and nitrogen losses among other treatments. Organic matter lost during the course of composting showed 30% losses in organic matter of chicken manure, followed by DPT + 50% CM, followed by DPTL while DPTL+ 25% chicken manure came in the last. In the same time humus content of the end product behaved differently, DPT+50 CM gave the highest values (23.2%), while date palm alone composted materials recorded the least content of humus, (10.50%), and this is mainly due to, the composting process of such materials needed longer time for maturation, and it is worth mentioning that mixing chicken manure with date palm tree leaves speeded up the compost maturity and improved its humus content and enhanced the compost quality due to the enrichment of the compost mix with rich materials of chicken manure specially nitrogen and phosphorus contents which narrowed the CNP levels.

Table 7, End product quality of finished compost after 120 days.

Parameter	Farm yard manure (FYM)	Date tree leaves	Chicken manure	DPT + 25% CM	DPT + 50% CM
Moisture (%)	22.0	27.1	25.0	24.2	26.0
Organic matter (%)	23.0	80.1	51.9	69.2	65.2
Total nitrogen (%)	0.57	0.69	3.2	1.77	1.82
Organic carbon (%)	13.37	46.46	30.1	40.1	37.8
C/N Ratio	23.4	67:3	9.4	22.6	20.7
Humus content (%)	3.2	10.50	20.10	21.40	23.20
Organic matter losses (%)	---	13.00	30.00	11.87	20.10

Table (8) reveals the microbial activities in the soil as affected by the addition of organic fertilizers from different compost mixes. In all treatments numbers of total plate counts showed higher numbers and activities over control. Enriching composted date palm leaves with chicken manure helped the microbial activity in composted date palm leaves as shown in table (8). Relation between microbial activity and soil fertility improvement due to addition of organic fertilizers, has been reported by several studies, [12, 27,28].

Addition of organic fertilizer to sandy soils showed enhancement of microbial population throughout the course of experiment for 180 days under date palm plantation in this experiment. Inoculation of soil by microorganisms increased the population of total plate counts. Interaction between organic matter from different compost materials improved the soil biota, and showed the highest biological activity of the soil against control (Table 8).

Table 8, Periodical changes of total plate counts (Log numbers) in treated soil.

Treatments	Time (days)					
	7	30	60	90	120	180
Control (FYM)	6.0	6.1	6.7	6.3	6.1	6.0
Composted date palm leaves	6.6	7.8	8.1	8.0	8.1	7.8
Composted chicken manure	6.6	8.2	8.4	8.8	8.5	8.4
Composted DPL + 25% CM	6.5	7.8	8.1	8.0	7.8	7.7
Composted DPL + 50 CM	6.8	8.8	8.9	9.1	9.0	8.8

Table (9) depicted the results of organic matter content in sandy soils under date palm trees as affected by addition of different composted materials. All treatments showed improvement of organicmatter contents in all treatments above control. Composted date palm tree leaves showed the highest contents of organic matter among other treatments. After six months of treatment the sandy soil content of organic matter was in the range of 0.45% for date palm leaves followed by 0.44% for the mix 50% chicken manure compost, while the control was only 0.26% in the sandy soil (Table 9).

Table 9, Periodical changes of organic matter content in treated sandy soil.

Treatments	Time (days)					
	7	30	60	90	120	180
Control (FYM)	0.31	0.29	0.29	0.28	0.26	0.26
Composted date palm leaves	0.51	0.48	0.48	0.46	0.45	0.45
Composted chicken manure	0.45	0.44	0.43	0.42	0.41	0.41
Composted DPL + 25% CM	0.48	0.46	0.44	0.43	0.43	0.42
Composted DPL + 50 CM	0.48	0.47	0.45	0.45	0.44	0.44

Table (10) depicts the effects of adding 25 kg of different organic fertilizers on date palm fruit productivity of Neghal variety. The results revealed that date palm trees responded positively with the addition of different organic fertilizers. All treatments increased above the control trees. The yield increased from 44.2, 56.5, 58.9, 55.5 and reach 72.0 kg per tree for control, then Composted date palm leaves, then Composted chicken manure, then Composted DPL + 25% CM, and Composted DPL + 50 CM respectively showed the highest yield. The results obtained in this experiment are in line with the studies done by several authors. The role of fertilizers and its effect on the growth of date palm trees and its yield quantity and quality has been studied and a positive relation between nutrients and tree growth are reported. Using composted organic fertilizers could be a natural input for increasing the growth of trees under the severe climate and desert soil, due mainly to the improvement of soil physical, chemical and biological properties as shown in this experiment. The results obtained in this experiment are in agreement with results obtained by, [29,30, 31, 32, 33, 34, 35, 36].

Table 10, Date fruit yield as affected by different compost types of 7 years old Neghal trees.

Treatments	Amounts in kg per tree	Increase above control
Control, (FYM)	44.2	-----
Date palm tree (DPT)	56.5	27.83
Chicken Manure (CMC	58.9	33.26
DPT + 25% CM	55.5	25.57
DPT +0 5% CM	72.0	62.90

In this experiment we found that, date palm tree wastes compost must be enriched with farm animal manures in order to enhance the composting process and speed up the biological reactions. In the same time soil amended with these compost materials showed positive effects in its fertility as well as date fruits yield [37, 38, 39, 40, 41, 42].

Conclusion

1. Co-composting of plant residues (Date palm leaves, DPL) with animal manures e.g. chicken manure has a positive role in the speed up of composting process and improving end product quality.
2. Bioconversion of farm wastes will fix the carbon in the soil and reduce the emission of hydrocarbon gases to air and will protect the environment.
3. Usage of compost will reduce the need for inorganic fertilizer usage, and this will contribute to protect the environment and reduce the fertilization cost.
4. Improving the soil physical, chemical and biological properties and buildup of organic matter and biota activity in sandy soils is mainly enhancing plant growth and plant yield.
5. Microorganisms are an important component of soil, and they influence the soil's health.
6. Co composting of farm wastes is a key for improving the environment and economics of the farming sector.

References

[1] W.H. Barreveld,: Date Palm Products in Food and Agriculture Organization of the United Nations. (1993).

[2] M. Mallaki, & R. Fatehi: “Design of a biomass power plant for burning date palm waste to cogenerate. (2014).

[3] FAO (Food and agriculture organization of the United Nations): Stat Crops Elements; Production Quantity, Items Dates, Statistical databases. Downloaded. (2018).

[4] K.R. Gray, K. Sherman, and A.J. Biddlestone: A Review of Composting—Part 1. Process Biochemistry, 6, 32-36. (1971).

[5] M.D.D. Bertoldi, G. Vallini, and A. Pera,: The Biology of Composting: A Review. Waste Management & Research, 1, 157-176. (1983).

[6] Eggerth, L.L. , Diaz, L.F., George M, Clarence G. (1993). Composting and Recycling Municipal Solid Waste (1993). Published January 29, 2019 by CRC Press, 318 Pages.

[7] E. Galiwango, A. Al Marzooky, A. Khaleel, M.M. Abu Omar, and N.S. Abdelrahman, Estimating Combustion Kinetics of UAE Date Palm tree Biomass using Thermogravimetric Analysis. Journal of natural science research, vol. 7, No. 12. N.S. (2017).

[8] B. Nakhshiniev, H.B., Gonzales, & K. Yoshikawa: "Hydrothermal Treatment of Date Palm Lignocellulose Residue for Organic Fertilizer Conversion: Effect on Cell Wall and Aerobic Degradation Rate", Compost Science & Utilization, vol. 20, no. 4, pp. 245-253.(2012).

[9] F. Hossain, S. Moustafa, F. El-Samiraie and M. Mahdi: Effect of nitrogen fertilization on growth, yield and fruit quality of dates grown in Saudi Arabia". Res. Bull No. 12. Ministry of Agriculture and Water, Research and Development, Saudi Arabia. (1979).

[10] R. Briones, L.Serrano, R.B.Younis, L. Jalil : Polyol production by chemical modification of date seeds. Industrial Crops and Product, 34(1):1035-1040, (2011).

[11] S.P. Mathur:. Composting Processes. p. 147-186. In A.M. Martin (Ed.). Bioconversion of Waste Materials to Industrial Products. Elsevier, London, New York. (1991).

[12] M.A., Badawi: Date Palm Trees Fertilization Requirements and Its Effect on Dates Yield, (Chapter 3 Date Palm: Composition, Cultivation and Uses, 36 pp. Beltane Bolduc (Editor) Series: Plant Science Research and Practices, BISAC: SCI073000 ISBN: 978-1-53616-676-7Categories: Nova, 2020; Plant Science Research and Practices.

[13] P.J. Gerber, H. Steinfeld, B. Henderson A. Mottet, C. Opio J. Dijkman A. Falcucci, G. Tempio Tackling climate change through livestock a global assessment of emissions and mitigation opportunities. Food and Agriculture Organization of the United Nations (FAO), Rome. (2013).

[14] R. Maja, D.V., Magdalena, A. Dana, B. Martin, M. Zbigniew, Valorization of Fish Waste Compost as a Fertilizer for Agricultural Use. Waste and Biomass Valorization (2019) 10:2537–2545. (2019).

[15] FAO, Food and Agriculture Organization: Waste management opportunities for rural communities from Phoenix Dactylifera-L, preparation of cellulose whiskers and natural rubber-based. (2007).

[16] C. Rajeswari, P. Padmavathy and S. Aanand: Composting of fish waste: A review, International Journal of Applied Research 2018; 4(6): 242-249 A B Rome, FAO Agricultural Services. (2018).

[17] J.R. Furr, & H.D. Barber: The nitrogen content of some date garden soils in relation to soil management practices. Ann. Rep. Date Growers' Inst., 27: 26-30. (1950).

[18] H.D. Chapman , and P.F. Pratt: Methods of analysis for soil, plants and water Univ. of California. Dir. Of Agric. Science Davis. (1961).

[19] A.O.A.C. Association of Official Analytical Chemists. Official Methods of analysis 12th Ed. A.O.A.C. Washington DC USA. (1975).

[20] C.A. Black, O.D. Evans; L.E. Ensminger J.L. White , F.E. Clark FE., and R.C. Dinaver: Methods of soil analysis part II. Chemical and microbiological properties, 2nd, Soil Sci., socities of Am. Inc., publications Madison Wisconsin, USA, 1573. RC. (1980).

[21] A.P.H.A., American public Health Association, Slandered Methods for Examination of Water And Waste Water, American Public Health Association 18th ed., Washington DC., USA. (1998).

[22] D.M.D.C.R. :Difco Manual,. Dehydrated culture Media and Reagents for microbiology, laboratories incorporated, Detroite, Mitchigan, 48232, USA, 621. (1985).

[23] M.A. Badawi: Humification of certain organic wastes during composting, Menofyia J. of Agric. Res. Vol. 22: No. 6: 1677-1685. (1997).

[24] F.J. Stevenson: Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients. John Wiley and Sons, New York (2005).

[25] C. G., Plaza A.M. Gascó; C. Zaccone; and F.T. Maestre: Soil organic matter in dryland ecosystems. In: Garcia C, Nannipieri P, Hernández T, editors. Futur soil carbon. Elsevier; p. 39–70. (2018).

[26] A. Zaid:. Production and Protection of date palm trees paper, No.: 156. Date Cultivation in South Africa. Information Bulletin No. 504; Compiled by the Fruit and Fruit Technology Research Institute, Department of Agriculture, Stellenbosch, RSA. 26pp. FAO, 156 . (2005).

[27] M. Alexander: Introduction to soil microbiology. 2nd ed. Jon Wiely & Sons. New York, USA. (1977).

[28] Badawi, M.A. and R. Obaidy: Effect of different organic fertilizer types on yield of organic dates fruits and its quality. The Blessed Tree, No. 1. 42-47.(2009).

[29] A.H. Shahein, A.M. Attalah, A.M., Kassim, H.A. and H.Aly: Effect of applying different organic and inorganic nitrogen sources on Zaghloul and Samany date cultivars on 11. Yield, fruit quality and fruit content of some pollutants. Date palm international conference. Alkasem, Saudi Arabia. (2003).

[30] M. Patidar and A.L. Mali: Residual effect of farmyard manure, fertilizer and biofertilizer on succeeding wheat (Triticum aestivum), Indian Journal of Agronomy 47(1):26-32.(2002).

[31] M.S.B. Salem, and I.A. Mousa: Effect of nitrogen and potassium fertilization on Hayany date palms in sandy soil. II. Yield and fruit quality". Egypt J. Appl. Sci., 4 (3): 406-415. (1989).

[32] A. E.K.S. Omar: Fertilization trials on some date palm varieties in Balteem district, Kafr El-Sheikh governorate". M.Sc. Thesis, Fac. of Agric. Kafr El-Sheikh, Tanta, Univ., Egypt.(1997).

[33] A.A. Al-Dejaili and J.A., Al-Dejaili: Fruits Production, Ministry of Higher Education Press, Mousil. (1989).

[34] B. Nixon, and C.A. Carpenter: Effect of the NPK fertilizer on the growth and yield of Date palm. Proceedings of the Date palm International Symposium Abu Dhabi, UAE, 19-21, (2006).

[35] M.A. Awad, A.A., Soaud, S.M. El-Konaissi, M.A., Badawi, and O.H., Eshkandi: Effect of Elemental Sulfur, Chemical and Organic Fertilizers on Nutrient Uptake, Yield and Fruit Quality of Date Palm trees (Phoenix dactylifera L.) c.v. 'Neghal' College of food and agriculture, UAEU annual conference, (2005).

[36] H. Elsadig, H. Aljuburi, A. Elamin and M. Gafar: Impact of organic manure and combination of N P K S, on yield, fruit quality and fruit mineral content of Khenazi date palm (Phoenix dactylifera L.) cultivar. Journal of Scientific Agriculture. 1. 335. 10.25081/jsa.2017.v1.848. (2017).

[37] M. Bacha, and A.A., Abo-Hassan: Effect of soil fertilization on yield, fruit quality and mineral content of Khadairi Date palm variety. Proceeding of the 1st Symposium on the DatePalm in Saudi Arabia. Al-Hassan: PP. 174-179. (1983).

[38] A. Bendhaou, Y. Habibi, H. Kaddami, & A. Dufresne: "Physiochemical characterization of Palm., (2009).

[39] P. Klein, and A. Zaid,. Date palm Fertilization: Updated information for modern Date cultivation in Namibia. Proceedings of the Date Palm International Symposium, Windhoek Namibia, 22-25 February 2000 P. 125. (2005).

[40] T.W. Embleton, And J.A. Cook,: The fertilizer value of date leaf and fruit stalk prunings. Ann. Rep. Date Growers' Inst., 24:18-19. (1947).

[41]. A.Faiad, M. Alsmari, M. M. Z. Ahmed * , L. M . Bouazizi , B. Alzahrani, and H. Alrobei, Date Palm Tree Waste Recycling: Treatment and Processing for Potential Engineering Applications, Sustainabiliyy, MDPI, 21, pp., (2022).

[42] M. Yakubu, M. Hayatu,U.E. Ubara ,A.I. Erumwenbibi H.A. Hamza, A.S. Shehu, Z. Ibrahim, Evaluation of the effects of Date palm waste Compost on Growth and Physiology of Date palm(*Phoenix dactylifera L.*) seedlings, Dutse Journal of Pure and Applied Sciences (DUJOPAS*), Vol. 6 No. 4 December 2020.*

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Utilization of Spent Detergent Solutions of the Specialized Agricultural Machinery Repair Shop

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Keywords: repair shop, spent detergent solutions, synthetic detergent solutions, water-oil emulsions, oil-containing sludges, lubricants, forms of reinforced concrete structures. used plate lubricants.

Abstract. The composition of spent detergent solutions of the repair shop of special agricultural machinery, which is based on the use of synthetic detergents, was studied. The technological scheme of oil preparation on the basis of the spent detergent solutions, water-oil emulsions and oil-containing slimes was developed. The obtained oil was used for lubrication of the forms of reinforced concrete structures.

Introduction

Currently, the treatment of effluents located in the basins of rivers flowing into the Azov and Black Seas is of particular relevance. Existing methods of wastewater treatment from oils, surfactants, heavy metal ions do not always provide a given treatment object or are difficult to operate. Therefore, there is a need to develop new reliable, efficient and environmentally friendly methods of the spent detergent solutions. Therefore, the study of the processing of spent detergent solutions and oil-containing wastewater from the mechanical shop of the repair and mechanical plant, formed in the areas of degreasing, diesel washing, steaming chambers of the vertical type, and determines the relevance of the chosen research direction.

Analysis of Publications

As a result of the analysis of production activity on the repair enterprises the oil-containing waste, dangerous for environment, is formed. However, aspects of their utilization are insufficiently covered in the literature. Taking into account the relevance of research, the authors of the article studied ways to reduce the amount of oil-containing waste for the disposal of spent plastics (PM). The technology of preparation of fine water-oil emulsion on the basis of the spent oil with high stability by means of a pneumatic radiator was developed. The resulting emulsion was a dispersed system in which the role of the dispersion medium was performed by spent PM, and the dispersed phase was water in the droplet form. The possibility of preparation of water-oil emulsion on the basis of spent plastic oils by means of shock waves generated by a pneumatic radiator was proved. Subsequently, the emulsion was used as an anti-adhesive coating applied to the surface of the molds in the manufacture of reinforced concrete products [1]. The authors propose the use of oil extracted from wastewater taken from contaminated areas on the oil platform of Alexandria Harbor, by the method of agglomeration and foam flotation for the calcium oil preparation. After flotation, the extracted oil showed a higher viscosity and a higher content of asphaltene compared to the primary base oil. In addition, the pop-up oil contained a high percentage of resins, which indicates the possibility of using reduced oil mixed with the primary base oil in the preparation of lubricants [2].

The method of spent detergent solutions and lubricants processing is considered in the engineering solution (patent) [3]. This method includes the supply of spent detergent solutions, lubricants and water to the apparatus, which is equipped with heating elements, heating of the substances, contained in the apparatus, before boiling, holding at boiling temperature until the separation of substances into fractions, subsequent shutdown of heating elements, settling substances until complete separation into fractions, supply of water under pressure into the apparatus from below and squeezing the oil through a nozzle into a container for collecting and sludge oil, squeezing through another nozzle soap into a container for collecting and sludge soap, pouring it into molds, drying for incineration followed by pumping remaining water and emulsion in a container for precipitation. The disadvantage of this method is the combustion of spent sludge, but not its processing, which in some cases poses an environmental hazard. In general, in the literature there is information on the manufacture of lubricants for metal molds, but without the use of wastewater generated at the enterprise. Such engineering solutions significantly expand the use of technology and ensure the environmental safety of water bodies and the environment [4, 5].

The authors, in works [6-9] considered the issues: utilization of sewage sludge of galvanic enterprises, ensuring environmental safety in the utilization of sewage sludge by obtaining refractories and treatment of liquid waste of galvanic production, by manufacturing refractories. In addition, an integrated approach allows for environmental and economic safety of water bodies in particular and the environment in general.

Materials and Methods

The purpose of the work is to conduct research aimed at the utilization of spent detergent solutions for repair production of agricultural enterprises. To achieve this goal, the following tasks were set:

1. By generalizing the experience of the work of circulating water supply systems, to carry out the research on utilization of the spent detergent solutions, water-oil emulsions and oil-containing slimes.
2. To carry out research on the change of weight of the oil put on a plate depending on concentration of emulsified oil in a washing detergent on the basis of synthetic detergents.
3. To develop the scheme of utilization of the spent detergent solutions, water-oil emulsions and oil-containing slimes which provide a full cycle in systems of circulating water supply.

Research Results

The main production cycle of engine repair at a repair and mechanical plant consists of external steaming of the unit in the steaming chamber with discharge of effluents generated in the prefabricated well. Next, the engine is disassembled into individual components and washed in cross washing machines with periodic discharge of spent detergent solutions into prefabricated tanks. After restoration of details assembly of the diesel engine and its test on stands is carried out. The necessary parts are electrochemically galvanized or chrome-plated. The main sources of industrial water consumption are the test area for diesels coming for repair, the galvanic section with galvanizing and etching lines of parts, the washing section.

Several local wastewater treatment schemes of the plant with utilization of valuable components and their reuse are offered. To do this, wastewater and waste technological solutions that are formed are divided into low-concentrated and concentrated. Low-concentrated wastewater includes wastewater from the diesel test site, flushing water from galvanic baths, discharges of reversible diesel cooling system. Studies have shown that low-concentration wastewater is contaminated with oil, diesel fuel, suspension, and heavy metal ions. The concentration of petroleum products reaches 1… 4 g/l.

Analysis of the composition of the spent cleaning solution allows us to conclude on the feasibility of its use as a lubricant for steel forms of reinforced concrete structures. For example, (Table 1) contaminants such as sodium carbonate, sodium silicate are accelerators of hardening of cement stone [10]; surfactant (syntamide) - plasticizes the concrete mixture [11, 12]; oils, petroleum products, resins have lubricating properties [13]. In this regard, it is possible to manufacture lubricants based on spent detergent solutions and motor oils in the construction industry.

Table 1. Chemical composition of the washing detergent "Labomid-203".

The main components	Chemical formula	Mass (weight) part [%]
Soda ash	Na_2CO_3	50
Sodium metasilicate	Na_2SiO_3	10
Trisodium phosphate	Na_2PO_3	30
Surfactant	syntamide	8
Alkyl sulfates	–	2

In the next table. 2 the content of contaminants in the spent detergent solution with the appropriate concentration in aqueous solution is shown.

Table 2. The content of contaminants in the spent detergent solution with a concentration of 8… 20 g/l in 15… 30% aqueous solution.

Organic impurities	Mineral impurities	The composition of the organic part				
		Oils	Resins	Oxyacids	Asphaltenes	Carbona-tes
58.5	5.9	33.9	14.2	1.2	1.0	1.1
59.0	5.85	33.55	14.15	1.25	1.15	1.10
57.55	5.35	32.25	13.75	1.05	1.10	1.15
93.5	39.2	68.1	49.2	13.2	16.6	29.2

The most optimal values are within the limits of organic impurities (58.5… 93.5) and mineral impurities (5.5… 39.2), and the composition of the organic part of the main components is at the level of average values (highlighted in bold).

An experiment was planned to produce the required amount of emulsified oil, the optimal amount of which varies in a wide range of concentrations of spent detergent solution. Spent MG-12 engine oil was taken as oil impurities, the volume of which was measured by a measuring cylinder and dispensed into «Labomida-203» solution with a concentration of 10… 40 g/dm^3. The temperature of the solution was recorded, which varied within 291… 318 °K. After stirring the model spent detergent solution for 10 minutes, the mixture was applied to a steel plate measuring 4 x 8 (cm). Previously, the steel plate was degreased in hot water, then acetone and dried in an oven at 323 °K. Weighing of the dry plate with the oil applied to it was carried out on analytical scales. The dispersion composition of the emulsified oil impurities was recorded by photographing the sample on a «Biolan» microscope with a magnification of several times (x 360)… (x 960). Due to the error of the experiment, which will make the evaporation from the plate of the washing solution, the rate of evaporation was determined by changing the weight of the plate for 10 ... 15 minutes. Studies have shown that the evaporation rate for different concentrations of detergent solution is constant over a given period of time (Fig. 1).

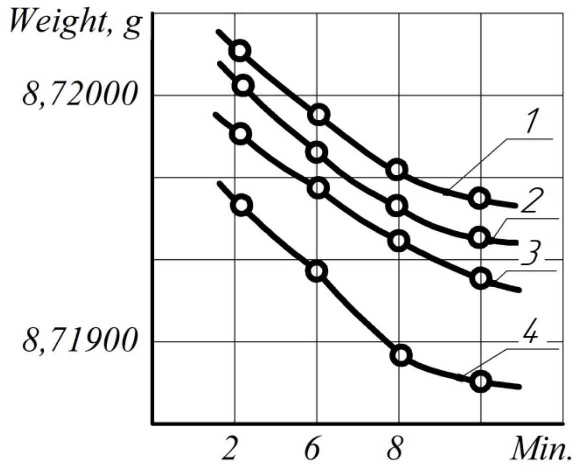

Fig. 1. Kinetics of change of weight of a plate with the put oil on the basis of the spent detergent solutions with concentration of emulsified oil (g/dm^3): 1 – 80; 2 – 120; 3 – 160; 4 – 200, depending on the mixing time.

4 minutes were taken as the estimated time interval for the whole series of the experiment. In addition, studies have shown that for the "Labomid-203" solution there is an optimal concentration of oil, which forms a film that provides high quality surface of reinforced concrete products. Semi-industrial tests of lubricant based on spent detergent solutions showed that its thickness should be in the range of 20 ... 100 μm. Studies have shown that the specified thickness corresponds to the concentration of emulsified oil 2 ... 10% in the spent detergent solutions based on the "Labomid-203" (Fig. 2).

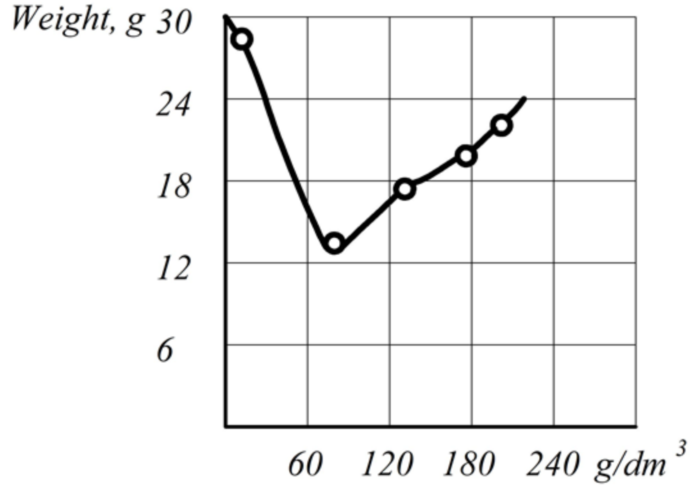

Fig. 2. Change in the weight of the oil applied to the plate depending on the concentration of emulsified oil in the detergent solution based on "Labomid-203" with a content of 40 g/dm^3.

Thus, the general technological scheme of preparation of oil on the basis of the spent detergent solutions will consist of the receiver of the spent oil which will arrive from a test site of diesel and a collector of oil sludge of a site of washing, a collector emulsifier of oil, the pump for mixing, the ejector device. The lubrication unit will work as follows. The spent detergent solution after preliminary clarification from coarse impurities is pumped by the pump into the collector-emulsifier, and spent oil is transported to the receiver of the spent oil which is connected to the ejector device. When the pump is running, part of the spent detergent solution will come from the discharge line to the ejector, in which the resolution is created. The volume of oil, which is set depending on the initial concentration of the detergent solution is mixed in the ejector diffuser and enters the suction pipe of the pump for additional mixing in the pump housing. This increases the high degree of oil emulsification, which improves the quality of oil preparation. Next, the mixture of oil and spent detergent solution enters the assembly-emulsifier through a perforated pipe installed in its lower part. Part of the demulsified oil floats to the top of the collector-emulsifier and through a perforated collecting pipe connected to the suction pipe of the pump is fed for re-mixing (Fig. 3).

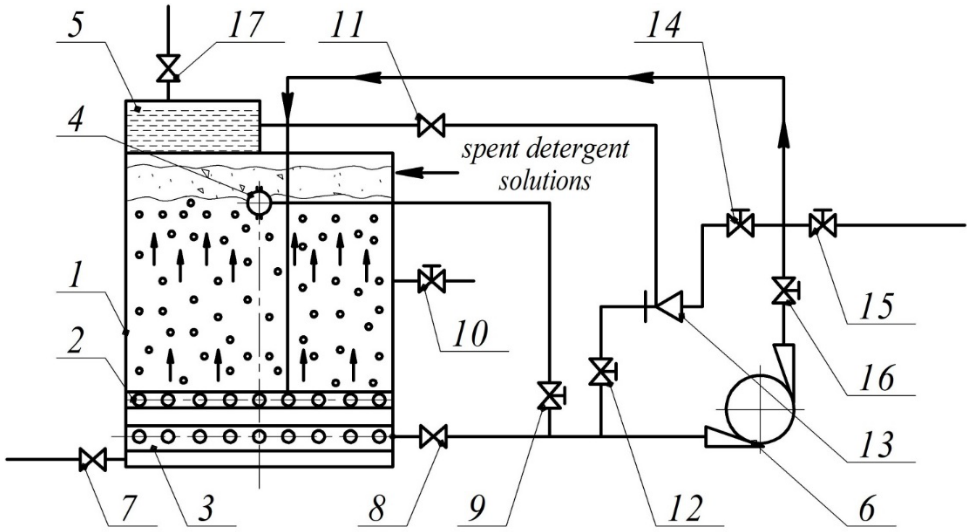

Fig. 3. Schematic diagram of oil preparation on the basis of spent detergent solutions, water-oil emulsions and oil-containing sludges: 1 – collector-emulsifier; 2 – distribution pipe; 3 – suction perforated pipe; 4 – pipe re-collection of demulsified oil; 5 – collector of spent oil and water-in-oil emulsions; 6 – centrifugal pump; 7 – sludge discharge valve; 8 – supply valve for cleaning solution; 9 – valve for repeated (additional) mixing; 10 – the valve for sampling; 11 – the valve of dosing of the spent oil; 12 – mixing supply valve for mixing; 13 – ejector device; 15 – valve oil supply for consumption; 16 – valve pressure line shutdown.

After oil preparation (mixing time 1...2 hours) the emulsion is transported to the car for transportation to the construction plant. General view of microheterogeneous impurities of oil in lubricant prepared on the basis of detergent solution with a concentration of 40 g/cm^3. The general view of microheterogeneous impurities of oil in the oil made on the basis of a detergent solution with a concentration of 40 g/cm^3 is presented in fig. 4.

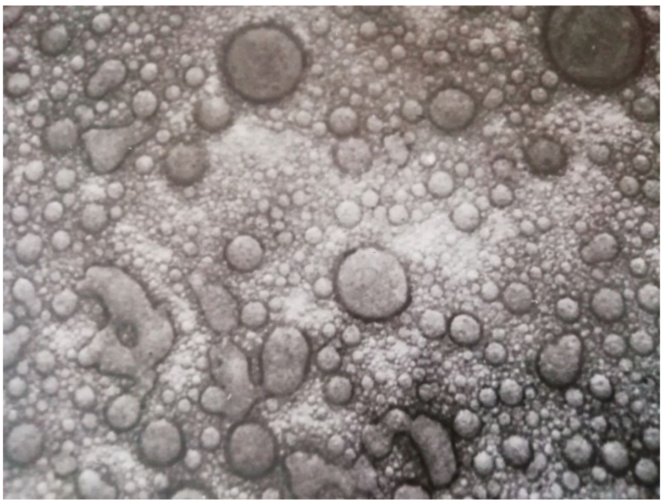

Fig. 4. The process of emulsification of oil impurities in oil based on "Labomid-203" with a concentration of 40 g/cm^3 of spent detergent and 120 g/cm^3 of spent engine oil with a stirring time of 20 minutes.

The main purpose of the obtained oil is to reduce or completely eliminate the adhesion of concrete to the formwork and facilitate the stripping of reinforced concrete structures. According to the principle of action of oil on the basis of the spent detergent solutions belongs to film-forming and slows down setting of a cement stone. The action of the oil is based on the formation on the entire surface of the formwork of a thin oil film covered with a layer of surfactant, which slows down the process of setting of the adjacent layers of concrete. As a result, by the time of stripping, the strength of these layers is negligible and the break occurs in part on the weak adjacent layers of concrete. In the future, the surface layers of concrete gain design strength and the quality of reinforced concrete structures is not reduced. The main requirement for oil is the release of products without damaging the molds and without deteriorating their physical and chemical properties. This is achieved by using spent detergent solutions with a concentration of the main component of the powder in the range of 30 ... 40 g/dm^3, the concentration of the oil base 80 ... 200 g/dm^3, pH-9.2 ... 10.8. The oil base must be evenly distributed in the oil. Control over the quality of oil preparation is carried out by applying it to a steel plate measuring 40 x 80 x 0.5 cm, pre-degreased with acetone and dried at 323 °K. After applying the oil, the control plate is placed vertically and for 1 minute the oil is drained onto the filtered paper. The plate is then placed on an analytical balance for weighing. The report is taken on the seventh sign in one minute for 4 minutes. Then the average value and difference of weights of a dry and oil plate (cf.) is defined. The difference (cf.) should be in the range of 0.02000 ... 0.03000 g, for spent detergents with a concentration of "Labomid-203" in the amount of 30 ... 40 g/dm^3 and an oil phase concentration of 100 ... 250 g/dm^3, pre-mixed for one hour.

The obtained oil is fireproof, does not cause corrosion of the metal surface, prevents contamination of pallets with concrete residues, non-toxic, has no pungent odor, provides mechanized application, holds well on the vertical surface of molds, does not flow under vibration, does not freeze at room temperature - 18 °C. Thus, the process of emulsification of oil impurities in the oil based on "Labomid-203" with a concentration of 40 g/cm^3 of spent detergent solution and 120 g/cm^3 of spent engine oil with a stirring time of 20 minutes.

Conclusions

Taking into account the experience of galvanic production waste management, their structural and physicochemical composition, as well as the results of research, it is possible to draw the following conclusions:

1. The scheme of recirculating water supply of the mechanical shop of the repair and mechanical plant was studied, which allows to optimize the technological parameters of the lubricant preparation process on the basis of spent detergent solutions and water-oil emulsions and oil sludges for lubricants of reinforced concrete products.
2. The composition of spent detergents based on "Labomid-203" with a concentration of 40 g/cm^3 of spent detergent and 120 g/cm^3 of spent engine oil with a stirring time of 20 minutes, possibly to lubricate the formwork of reinforced concrete structures.
3. The scheme of utilization of the spent detergent solutions, water-oil emulsions and oil-containing slimes with the main component of powder within 30 ... 40 g/dm^3, concentration of oil base of 80 ... 200 g/dm^3, pH-9.2 ... 10 was developed 8, which allows to optimize the operation of water treatment equipment in the circulating water supply system of the enterprise.

References

[1] V. Ivanov, V. Donchenko, V. Lopata, Preparation of emulsions based on emulsions based on spent greases. Problems of tribology. 80(2) (2016) 63–68.

[2] M.M. Soliman [et al.], Oil recovery by flotation from waste water as a source of lubricating grease. Triblogy and Lubrication Engineering : the materials of the 14 International Colloquium Tribology, Ostfildern, Jan. 13–15, 2004 . 3 (2004) 1533–1543.

[3] P.I. Troyan, Russian Patent. 2007107155/044 (2007).

[4] M.A. Nirkov, V.T. Procishin, Ukraine Patent. 200706001 (2007).

[5] O.V. Shaposhnik, O.D. Stahurskii, O.O. Makedonskii, G.F. Terehova, V.I. Vavrik, T.O. Borodenko, S.G. Shafranova, Ukraine Patent. 2001117838 (2002).

[6] L. Chernyshova, S. Movchan, S. Epoyan, Utilization of galvanic enterprises sewage. Material Science Forum. 1038 (2021) 282–289.

[7] L. Chernyshova, S. Movchan, S. Epoyan. Utilizaciya osadiv stichnih vod galvanichnih pidpriemstv: materiali mijnarodnoï naukovo-praktichnoï konferenciï «Problems of Emergency Situation», Harkiv, 20 travnya, 2021. (2021) 374–375.

[8] S. Movchan, L. Chernyshova. Zabezpechennya ekologichnoï bezpeki utilizaciï osadiv stichnih vod shlyahom otrimannya vognetriviv. Naukovii visnik Tavriiskogo derjavnogo agrotehnologichnogo universitetu: elektronne naukove fahove vidannya. 11(1) (2021) 11.

[9] L. Chernyshova, S. Movchan. Povodjennya z vidhodami galvanichnogo virobnictva shlyahom vigotovlennya vognetriviv. Eko Forum (2021): zbirka tez dopovidei V specializovanogo mijnarodnogo Zaporizkogo ekologichnogo forumu, 14–16 veresnya, 2021. (2021) 298–300.

[10] V.I. Goc, Betoni i budivelni rozchini, Kiev, 2016, 567 s.

[11] Dobavki dlya betoniv. Metodi viznachennya efektivnosti. Kiev, 1999, 38 s.

[12] Pravila zastosuvannya himichnih dobavok u betonah i rozchinah. Kiev, 1999, 60 s.

[13] M.V. Zavoloka, Monolitne domobuduvannya. Odessa, 2002, 222 s.

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Innovative Technology for Clearing Detergent Solutions after Car Washing while Making Environmentally Friendly Managerial Decisions

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Keywords: detergent solution, suspended solids, oil products, synthetic surfactants, car wash, environmentally friendly managerial decisions.

Abstract. This article outlines an innovative solution for clearing detergent solutions after car washing. Managerial decision-making process being environmentally friendly is based on experimental data. The focus of the research is the development of a mobile car wash and dryer with regeneration of detergent solutions, which ensures environmental safety. The calculation of the prevented damage from the discharge of detergent solutions after car washing into water bodies was carried out as a result of an effective environmental solution. The economic efficiency of the proposed introduction of a mobile car wash with the regeneration of detergent solutions is given.

1 Introduction

The mainstream of economic theory of the last decade is the concept of "green economy". Under this economic model, natural capital is the main economic asset [1], which seeks to reduce waste, limit resources and energy for production. The elements of the concept of "green economy" are the following: transition to a low-carbon economy → resource efficiency → social integration [2, 3].

The technology of clearing detergent solutions after car washing contributes to sustainable and environmentally sound restoration of the environment, which is considered within the framework of the green economy model. This conclusion is supported by analytical data, which indicate that car wash wastewater is a significant source of environmental pollution due to the diversity and high concentration of pollutants contained in it. These toxic wastewaters contain heavy metals that can end up in surface and groundwater [4]. Innovative solutions, such as the technology of clearing detergent solutions after car washing with further water reusing, can provide an environmentally friendly process that is both efficient and affordable.

In a comparative analysis, the main pollutants of wastewater after car washing were identified: suspended solids and oil products. At the same time, the concentration of suspended solids in them depends on a large number of factors: the type of vehicle, its size, the nature of the road surface, seasonal conditions, the composition of soils in the area of operation, the frequency of washing and the type of car wash used.

Chemical analytics shows that used detergent solutions after car washing contain suspended solids, oil products and synthetic surfactants. Among these components, oil products and synthetic surfactants represent the highest environmental hazard [5].

Most operating car washes with their large and irrational water consumption, imperfect clearing systems (and sometimes their complete absence), imperfect and uneconomical technological equipment cannot meet modern requirements any longer. In addition, stationary car washes, able to carry out the process of washing and drying vehicles in one pass, cannot be close to places of vehicles congestion, and mobile ones, which can be used in the field, are characterized by low productivity and a number of operations performed, they require a large amount of overall equipment and they are difficult to operate [6, 7].

Taking into account that motor vehicles make trips to different areas and on the surface of its wheels and body there can be all kinds of contaminants, including highly toxic ones, it is essential that the detergent solution clearing system provides high sorption capacity and has neutralizing qualities. Moreover, car washes are needed for sanitary protection zones of resort areas and protected areas, areas with a special epidemiological regime of functioning (bird flu, anthrax and other animal diseases), camping sites, separate parking lots, for washing cars under adverse conditions before entering large industrial cities, etc. In some cases, it becomes necessary to use car washes in the field without fresh water and sewage.

2 Mobile Car Wash and Dryer with Regeneration of Detergent Solutions

Currently, both in our country and abroad, there is a wide variety of car washes. This circumstance is explained by the growth of the car park, the deterioration of the environmental situation, the tightening of penalties for enterprises that discharge uncleared wastewater, the increase in water price and the shortage of fresh water in Ukraine [8, 9, 10].

Therefore, based on the experimental studies [11], a mobile unit for washing and drying cars with the regeneration of detergent solutions was developed, which ensures environmental safety.
The proposed mobile unit for washing and drying cars with the regeneration of detergent solutions is shown in Fig. 1 (I - general view; II - schematic diagram) [12].

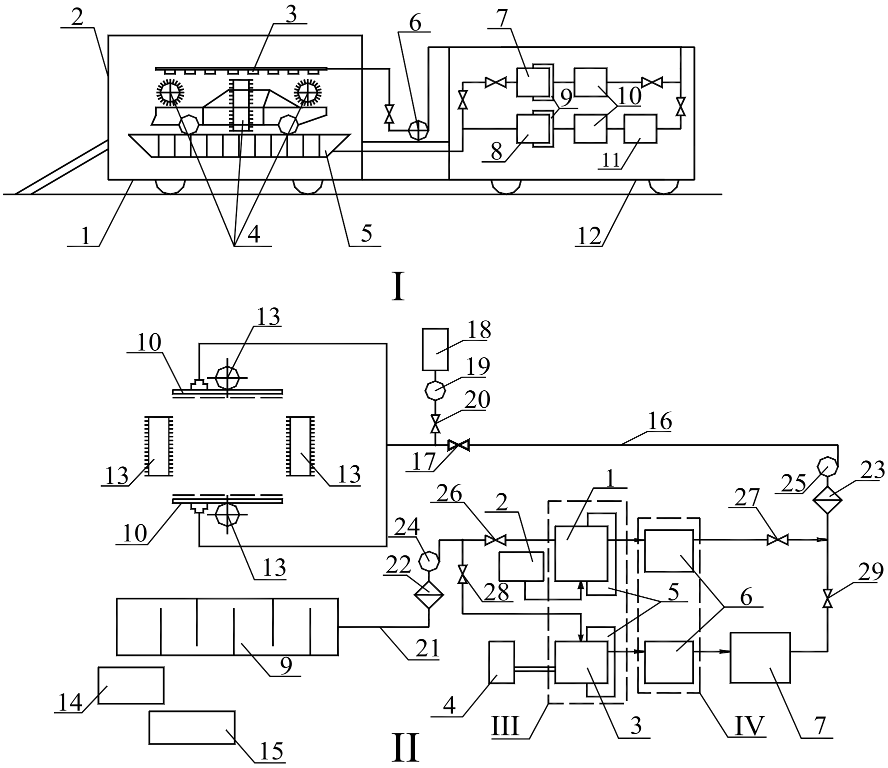

Fig.1. Mobile car wash and dryer with regeneration of detergent solutions

The unit includes flotation cell 1, equipped with a compressor 2; electric coagulator 3 with electric current rectifier 4; froth collectors 5, shelf settlers 6, storage tank 7 mounted on chassis 8. Tray 9 and shower collector 10 mounted on chassis 11 are equipped with an awning or frame 12 and rotary brushes 13 on rotary consoles driven by an electric motor 14 from a remote control 15 operation of the unit. Cleared water pipeline 16 is connected to the shower collector 10, with a shut-off valve 17. A heater 18 with a fan 19 and a valve 20 is located on its branch. The flotation cell and electric coagulator are connected with wastewater pipeline 21 with a tray 9. Wastewater and cleared water pipelines are equipped with filters for clearing 22 and after-clearing 23, exhausting 24 and washing 25 pumps. The flotation cell, through a shut-off valve 26, is connected to the wastewater pipeline. The shelf settler 6 is connected to the cleared water pipeline by a shut-off valve 27. The wastewater pipeline is connected to the electric coagulator by a bypass pipeline with a shut-off valve 28. The storage tank 7 is connected to the cleared water pipeline by a shut-off valve 29. The power supply is not shown in the scheme. It is installed directly next to the cabin of the vehicle.

The operation of the unit is carried out as follows. The vehicle goes upon chassis 8. The power supply is turned on. From the remote control 15, the washing pump 25 is turned on and water from the storage tank 7, through the cleared water pipeline 16, is supplied to the shower collector 10; the shut-off valve 27 and the valve 20 are closed and the shut-off valve 29 is open. Then, from the remote control 15, the electric motor 14 is turned on, which drives the rotary brushes 13. The contaminants washed off by the detergent solution get into the tray 9, from where, as it is filled, with the exhausting pump 24, through the cleaning filter 22, flow through the wastewater pipeline 21 into the flotation cell 1, where the detergent solution is saturated with air due to the compressor 2. The shut-off valve 28 is closed.

Clearing by flotation is accompanied by a decrease in the concentration of oil products, synthetic surfactants. The resulting flotation concentrate is collected in the froth collector 5. After flotation clearing, the detergent solution enters the shelf settler 6 and, through the after-clearing filter 23, by the washing pump 25, through the cleared water pipeline 16, gets into the shower collector 10. At the same time, shut-off valves 17 and 27 are open; valves 20 and 29 are closed.

For after-clearing detergent solutions to meet the requirements for the composition of industrial wastewater discharged into the city sewer, electrochemical clearing in an electric coagulator 3 is needed. To do this, contaminated detergent solutions are fed through a bypass pipeline, through a shut-off valve 28, into an electric coagulator 3, for the further clearing. The coagulated impurities, in the form of foam, are brought to the surface of the liquid column and then discharged into the froth collector 5, and the cleared detergent solution is fed into the shelf settler 6, where coagulation products are separated. Cleared water gets into the storage tank 7. Block III provides the process of electric flotocoagulation, and block IV provides the settling process.

Cleared water obtained as a result of electrochemical clearing is used for washing cars. To do this, it is fed from the storage tank 7, through the after-clearing filter 23, by the washing pump 25, through the cleared water pipeline 16, to the shower collector 10.

The process of drying vehicles can be carried out simultaneously with the process of clearing detergent solutions. At the same time, before turning on the heater, the water from the shower collector 10, in order to avoid getting it on the heating devices, through the cleared water pipeline 16, is drained into the storage tank 7, after that the shut-off valve 17 closes and the valve 20 opens. The electric motor 14 is turned off on the remote control 15, the rotary brushes 13 are turned off and retracted from the car body. The heater 18 and the fan 19 are turned on. The heated air enters the collector 10. Through the nozzles of the collector 10, the car body is blown. At the end of the drying process, the heater 18 is turned off, the valve 20 closes and the shut-off valve 17 opens. The unit is prepared for the washing process of the next car.

The peculiarities of the proposed unit are [12]:

– separation of the process of clearing detergent solutions for initial and final car washing;

– the use of detergent solutions in the flotation clearing scheme provides a decrease in the concentration of oil products and synthetic surfactants according to the requirements for the quality of reused water for car washing;

– the use of an improved design of an electric coagulator for after-clearing of detergent solutions in the scheme following the requirements for the composition of industrial waste water discharged into the city sewerage and the use of cleared water for washing cars.

The use of an electrochemical clearing device in the detergent solution clearing unit and the combination of the drying unit with the washing shower collector allows to reduce the time for the detergent solution clearing process and for processing a vehicle, which generally leads to saving energy consumption and increasing the efficiency of the unit.

The proposed layout of units and systems of water circulation circuits, which allows clearing solutions formed after washing vehicles, both during washing or drying, and autonomously in a closed circuit, reduces water consumption, and therefore reduces operating costs. Furthermore, the proposed unit, made on a mobile chassis, allows reducing construction costs, reducing the complexity of installation and using it in campsites, gas stations or elsewhere, there is a flat area needed that allows cars to drive on the washing box chassis. During the operation of the unit, no water mains and sewerage are required.

3 Economic and Social Aspects of the Technology of Clearing Detergent Solutions with Reused Water

Large amounts of pollutants get into the environment, primarily surface water bodies with reused waters.

Due to the fact, that each enterprise, depending on the adopted production technology, can discharge various pollutants into water bodies, a direct comparative analysis of surface water pollution by different water management facilities is impossible [13].

As a rule, in such cases, complex indicators are used [14]. Complex indicators are calculated by integrating heterogeneous data that comprehensively characterize the analyzed process. The methodology for calculating a complex indicator should take into account both the characteristics of the object and the purpose of the analysis. The peculiarity of complex assessments of a set of complex objects is the possibility of conducting a comparative assessment of these objects.

To conduct a comparative analysis of the impact of pollutant discharge after car washing in administrative and territorial units and separate economic facilities of the Kharkiv region, a generalized discharge indicator (GDI) [13, 15] was used, which was calculated by the formula,

$$GDI = \max \cdot \sum_{i=1}^{n} \frac{m_i}{MPC_i} \quad (1)$$

where

max – the amount of used detergent solution for car washing;

m_i – the amount of the i-th pollutant (suspended substances and oil products) in the discharge;

MPC_i – maximum permissible concentrations of pollutants (suspended substances and oil products) for water bodies for fishery use.

Since the content of synthetic surfactants in detergent solutions after their electrocoagulation clearing is significantly lower than required for the maximum permissible concentration indicator, the concentration of synthetic surfactants was not taken into account when calculating the generalized discharge indicator.

The generalized discharge indicator is a complex indicator that can be used for comparative analysis of the influence of different water users on surface water bodies. In its physical meaning, the generalized discharge indicator shows how much clean (fresh) water must be used to dilute the discharge of all pollutants to a safe (maximum permissible) concentration, taking into account the synergy of different pollutants with the same harmful effect, without taking into account self-clearing processes. The generalized discharge indicator can be calculated for an individual water user enterprise, in total for a district, in total for a water body or part of it.

Table 1 shows the initial data for calculating the prevented damage from the discharge of detergent solutions after car washing into surface water bodies.

When conducting studies of detergent solutions, we took into account only average amount of main contaminants in solutions that included five different types of synthetic surfactants ($NavVavSav_n$).

The following detergent solutions were used for the study: $NavVavSav_1$ containing sodium salt of secondary C_{10}-C_{18} alkyl sulfates; $NavVavSav_2$ containing Labomid 101; $NavVavSav_3$ containing Synthamide-5; $NavVavSav_4$ containing sodium salt of secondary C_{10}-C_{18} alkyl sulfates + 12% monoethanolamine; $NavVavSav_5$, containing triethanolamine salt and NavVav without synthetic surfactant.

Table 1. Input data for calculating the prevented damage from the discharge of detergent solutions into surface water bodies

Indicators	Concentration of dissolved substances after electrocoagulation clearing in various detergent solutions, [mg/dm^3]						Maximum allowable concentration, [mg/dm^3]
	NavVavSav$_1$	NavVavSav$_2$	NavVavSav$_3$	NavVavSav$_4$	NavVavSav$_5$	NavVav	
Suspended solids	1.05	1.55	1.16	0.86	1.15	2.04	0.25
Oil products	0.92	0.82	0.80	0.64	0.93	0.76	0.05
Synthetic surfactants	no more than 0,01					–	0.5

In accordance with ratio (1) and based on the data in Table 1, the amount of clean (fresh) water required to dilute 5 m^3 of the studied detergent solutions after car washing NavVavSav$_{1\text{-}5}$ and NavVav, before they are discharged into water bodies is as follows:

$GDI_1 = 5 \cdot (1.05/0{,}25 + 0.92/0{,}05) = 113$ m^3 $GDI_2 = 5 \cdot (1.55/0.25 + 0.82/0.05) = 113$ m^3

$GDI_3 = 5 \cdot (1.16/0.25 + 0.80/0.05) = 103.2$ m^3 $GDI_4 = 5 \cdot (0.86/0.25 + 0.64/0.05) = 81.2$ m^3

$GDI_5 = 5 \cdot (1.15/0.25 + 0.93/0.05) = 116$ m^3 $GDI_6 = 5 \cdot (2.04/0.25 + 0.76/0.05) = 116.8$ m^3

From the results of the calculation, it follows that the highest consumption of fresh water is necessary to dilute the detergent solution NavVavSav$_1$ containing the sodium salt of secondary C_{10}-C_{18} alkyl sulfates, and the smallest one is for the detergent solution NavVavSav$_4$ containing the sodium salt of secondary C_{10}-C_{18} alkyl sulfates + 12% monoethanolamine. As for the other studied solutions, including the solution without a synthetic surfactant, the fresh water consumption for them is approximately the same.

It is noted that with the help of a generalized discharge indicator, it is possible to analyze the degree of reused water clearing from pollutants, i.e. assess the performance of water clearing facilities.

To carry out such an analysis, the generalized indicator of pollutant discharges according to the generalized indicators of discharges of a water user enterprise that discharges them into a certain water body must be divided by the value of the corresponding volume of wastewater. As a result, we obtain a complex indicator of the conditional multiplicity of dilution of reused water (MDRW). The dilution ratio of circulating water is a complex indicator that is used only for comparative analysis. In terms of physical meaning, the dilution ratio of reused waters is analogous to the generalized concentration of all pollutants, taken into account in the maximum allowable concentration, in reused waters.

The complex indicator of the conditional multiplicity of dilution (MD) of various detergent solutions after car washing is, respectively:

$MD_1 = 113/5 = 22.6$ $MD_2 = 113/5 = 22.6$ $MD_3 = 103.2/5 = 20.6$

$MD_4 = 81.2/5 = 16.2$ $MD_5 = 116/5 = 23.2$ $MD_6 = 116.8/5 = 23.4$

The results of the analysis of this indicator for different types of detergent solutions show that the largest, approximately equal generalized dilution ratio to the maximum permissible concentration, is typical for detergent solutions NavVavSav$_1$, NavVavSav$_2$, NavVavSav$_5$ and NavVav, and the least one is for detergent solution NavVavSav$_4$.

The indicator of cost efficiency for the introduction of a mobile unit for washing and drying cars with the regeneration of detergent solutions is the ratio of the total annual economic effect to the sum of the operating costs and capital investments that caused this effect [16]:

$$E = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[E_{ij} / \left(Oi + EnCi \right) \right] \quad (2)$$

where

E_{ij} is the economic effect of the i-th type on the j-th object;

O_i is annual operating costs;

C_i is capital investments for a group of objects;

E_n is the normative coefficient of efficiency of capital investments for environmental purposes in the national economy.

In accordance with the methodology [16], the calculation of economic efficiency when introducing a new technology is determined by the formula:

$$E_1 = (C_1 \cdot E_n + O_1) - (C_2 \cdot E_n + O_2) \quad (3)$$

where

C_1, C_2 are capital costs for the compared clearing method and the proposed one;

E_n is normative coefficient, $E_n = 0.15$ [16];

O_1, O_2 are operating costs for the similar and recommended unit, respectively.

For comparison of capital and operating costs for the proposed mobile car wash, a stationary car wash unit at ATE-12328 in Zaporizhzhia was taken as similar. Comparative costs of the developed unit and the similar one are given in Table 2.

Table 2. Comparative costs of the developed mobile unit for clearing detergent solutions after washing cars, and the similar unit

Investments	Costs for compared units, [UAH]	
	similar	developed
Capital	101232	30000
Operational	67100	63200

The table shows that the capital and operating costs of the proposed mobile car wash are much lower than the cost of the similar one. This is explainable due to the fact that a mobile car wash does not require capital construction costs, and during its operation, natural gas and diesel fuel are used as energy resource.

Savings on a mobile car wash due to the reuse of water will be determined by the

$$E_2 = Q_w \cdot C_3 \quad (4)$$

where

Q_w is the amount of consumed fresh water (5 m^3/hour);

C_3 is the cost of fresh water (UAH 16.08).

The economic efficiency from the introduction of technology and unit for clearing and regeneration of detergent solutions (E_r) at the given costs will be:

$$E_r = E_1 + E_2 \quad (5)$$

Using ratio (3), we determine the economic efficiency for capital and operating costs

$$E_1 = (101232 \cdot 0{,}15 + 67100) - (30000 \cdot 0{,}15 + 63200) = 14585 \text{ UAH}$$

Savings due to the reuse of water for a mobile wash at detergent solution use with flow rate of 5m^3/h, a wash operation mode of 5280 hours/year and a water use coefficient equal to five, will be determined by ratio (4):

$E_2 = 5 \cdot 5280 \cdot 16{,}08 - 5 \cdot 5280/5 \cdot 16{,}08 = 339610$ UAH./year

The expected economic efficiency from the introduction of technology and unit for clearing and regeneration of detergent solutions after car washing (E_r) according to given costs using ratio (5) will be:

$E_r = 14585 + 339610 = 354\ 195$ UAH./year

However, the real value of efficiency is greater, because dilution ratios of various detergent solutions after car washing, payment, fines and other costs are not fully taken into account.
According to the monitoring, the annual total amount of detergent solutions after car washing, excluding car washes for own needs, throughout Ukraine is 7300 thousand cubic meters, and in the Kharkiv region it is 470 thousand cubic meters. If we evaluate the reuse of water, then the economic efficiency only in the Kharkiv region, for all types of washes, can be

$E = 470000 \cdot 16{,}08 - 470000/5 \cdot 16{,}08 = 6\ 046\ 080$ UAH./year

4 Environmentally Friendly Decision Making

Environment has received increased attention at the national and regional levels in recent decades. For making environmentally friendly managerial decisions, such interdependent and interrelated elements as the enterprise and the environment are important: The development of the theory and practice of management in the field of ecology and environmental protection has led to the emergence of environmental management [3]. The environmentally friendly managerial decision is a complex process that is implemented while the manager takes into account environmental considerations for the planned activity. With such a conceptual approach, nature can be put into the center of innovative approaches to management decision-making by business entities. When implementing environmentally friendly solutions at an enterprise (wash), we propose to use a morphological model: each environmental management decision can be graphically represented as a cube, the sides of which will be interconnected and interdependent production processes, elements, their components, and one of the components of the environment.

In addition, any “environmental” decision must be based on a perception of the “significance” of expected environmental impacts. Therefore, in this study, the calculation of the economic efficiency of the introduction of innovative technology for clearing detergent solutions after car washing can be compared with the expected social and economic benefits from it. A mobile car wash allows performing a number of social tasks in conditions while other technologies and equipment cannot do it. How, for example, to evaluate the cleaning of vehicles in an emergency zone, where there are no washing systems, and it is impossible to let cars out of the zone unwashed. How to evaluate the efficiency of the system in conditions where there is no source of water and electricity, and the proposed system can work in such conditions.

The adoption and implementation of environmentally friendly managerial decisions based on innovative technology for clearing detergent solutions after car washing contributes to the implementation of the concept of “green economy”. Thus, natural capital seeks to reduce waste, limit resources and energy for production. Simultaneously, the use of an electrochemical clearing device in detergent solution clearing unit and the combination of the drying unit with the shower collector leads to saving energy consumption and increasing the efficiency of the unit.

Any economic entity always has limited resources for the implementation of its own business processes or seeks to minimize them. This leads to a targeted reduction of environmental costs by enterprises. The proposed layout of the units and systems of the water circulation circuits in the proposed unit reduces water consumption, and therefore reduces operating costs.

Moreover, the proposed unit is installed on a mobile chassis, which allows reducing the cost of construction work, reducing the complexity of installation and using it in simplified conditions of human activities.

Summary

The problem of optimization and management decision-making in environmental safety can be solved only in close cooperation with nature management, social ecology, and the economy. Environmental solutions based on the developed technological scheme of a mobile unit on a trailer platform for washing and drying cars with regeneration of detergent solution are actions aimed at the protection, sustainable management and restoration of ecosystems in a way that faces social problems in order to provide both human and territories well-being.

The developed technological scheme of a mobile unit on a trailer platform for washing and drying cars with regeneration of detergent solution is supposed to be used in sanitary protection zones of resort areas, areas with a special mode of operation, car camping, etc. The unit provides the separation of the process of clearing detergent solutions for car washing, includes flotation and electrocoagulation clearing of solutions, which make it possible to reduce the concentration of oil products and synthetic surfactants to follow the requirements for the composition of water discharged into the city sewer and reused for washing cars.

Economic calculations of the environmental effect have shown that the introduction of the developed technology for clearing detergent solutions after car washing will minimize the discharge of polluted effluents into the sewer, reduce the cost of fresh water due to its reuse.

The most important social effect from the introduction of developments considered is the reduction of damage to the environment and human health from the discharge of non-cleared waste detergent solutions after car washing, as well as in emergency situations of technogenic and epidemiological origin.

References

[1] More information about the concept of green economy: Information on www.unenvironment.org/resources/publication/shades-green-introduction-green-economy-parliamentarians-issues-brief

[2] Supporting resource efficiency: Information on https://www.unep.org/regions/asia-and-pacific/regional-initiatives/supporting-resource-efficiency

[3] O.V. Portna, N.Yu. Iershova, Eco-management of organizations within the green economy system. Acta Innovations, **35** (2020) 81–94.

[4] Analitychnyj ogljad stanu tehnogennoi' ta pryrodnoi' bezpeky v Ukrai'ni za 2016-2019 roky – UkrNDICZ: Information on https://undicz.dsns.gov.ua/ua/Analitichniy-oglyad-stanu-tehnogennoyi-taprirodnoyi-bezpeki-v-Ukrayini.html 2020 [in Ukrainian]

[5] J. Hansen, Cleaning up the dirty words of car washing. Modern Car Care. 4(1) (2002).

[6] L. A. Muratova, A. Ja. Gol'din, P. V. Molodov, Vodopotreblenie i vodootvedenie avtotransportnyh i avtoremontnyh predprijatij, Transport, Moskva, 1988 [in Russian].

[7] V. M. Hvat, A. V. Roshkevskaja, T. Ja. Zaslavskaja, Kontrol' za vypuskom stochnyh vod avtotransportnyh predprijatij v vodnye obekty i kompleks sooruzhenij dlja ih ochistki. Jekonomicheskie, tehnicheskie i organizacionnye osnovy ohrany vod: sbornik nauchnyh trudov, Har'kov, 1986 [in Russian].

[8] F. Talebzadeh, C. Valeo, R. Gupta, C. P. Constabel, Exploring the Potential in LID Technologies for Remediating Heavy Metals in Carwash Wastewater. Sustainability, **13(16)** (2021) 7-27.

[9] H. Janik, A. Kupiec, Trends in Modern Car Washing. Paul J. Environ. Stud, **16(6)** (2007) 927–931.

[10] I. Monney, E. A. Donkor, R. Buamah, Clean vehicles, polluted waters: empirical estimates of water consumption and pollution loads of the carwash industry. Helion, **6(5)** (2020).

[11] N. A. Bukatenko, Usovershenstvovanie processov mojki avtomobilej s obespecheniem jekologicheskoj bezopasnosti i racional'nogo ispol'zovanija vodnyh resursov: dis. na soiskanie uchen. stepeni kand. tehn. nauk, Har'kov, 2009 [in Russian].

[12] V. V. Berezuc'kyj, N. O Bukatenko, Patent 34249 Ukrai'ny, MPK B 60 S 3/00. Peresuvna ustanovka dlja myttja ta sushinnja avtomobiliv z regeneracijeju myjnyh rozchyniv. Zajavnyk ta patentovlasnyk Nacional'nyj tehnichnyj universytet "HPI". № u 2008 00216 [in Ukrainian].

[13] Ekologichnyj atlas Harkivs'koi' oblasti. Nauk. kerivnyk rozrobky: Je. L. Makarovs'kyj ta in., UkrNDIEP, Harkiv, (2005) [in Ukrainian].

[14] E. L. Makarovskij, Ocenka prirodno-resursnogo potenciala v regional'nom kadastre (na primere Har'kovskoj oblasti Ukrainy). Geografija i prirodnye resursy, **1** (2004)76-81 [in Russian].

[15] Metodicheskie ukazanija o sostave, soderzhanii, porjadke razrabotki, soglasovanija, utverzhdenija i utochnenija shem kompleksnogo ispol'zovanija i ohrany vodnyh resursov (L. I. Polad-Zade, A. K. Kuzin, E. L. Makarovskij i dr.), Sojuzvodproekt, Moskva, 1987 [in Russian].

[16] D. S. Shhavelev, M. F. Gubin, V. L. Kuperman, M. P. Fedorov, Jekonomika gidrotehnicheskogo i vodohozjajstvennogo stroitel'stva, Strojizdat, Moskva, 1986 [in Russian].

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Catalytic Activity of Fibrous Complexites

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Abstract. The ecological situation in the world requires the solution of environmental problems associated with the processes of wastewater treatment, hydrogen sulfide pollution of various industrial facilities in order to remove such harmful impurities. The unpleasant odor that appears in industrial and adjacent waste processing areas is a constant concern for the protection of the environment. To solve these problems, it is advisable to use selective sorbents - complex. The introduction of metal ions into complex fibers due to the formation of a coordinated bond between the groups of the metal and the polymer ligand gives high molecular weight complex compounds. The operational and selective properties of the materials based on high-molecular-weight complex compounds can be determined by the type of metal ion introduced into macromolecules, the nature of the polymer chain, and thermodynamic stability. By changing the action of the above factors, complexites can be synthesized for use as highly selective catalysts for various chemical processes. The paper presents data on the catalytic activity of fibers with Cu^{2+}, Co^{2+}, Ni^{2+} ions with complexing fibers containing carboxyl, amidoxime, hydroxamic groups, using the example of the decomposition of hydrogen peroxide and oxidation of H_2S, Na_2S. An inhibitory effect on the oxidation of fiber functional groups in the pH range 5.5 - 12.5 was revealed. The operational and selective properties of materials based on complexites can be determined by the type of metal ion introduced into the macromolecules, by the nature of the polymer chain. By changing the action of the above factors, complexites can be synthesized to be used as highly selective catalysts for various chemical processes. It was found that the catalytic activity of the complex depends on pH, the stereochemistry of the coordination centers in the fiber matrix and significantly exceeds the activity of model low-molecular-weight complex compounds.

1 Introduction

The ecological situation in the world requires urgent solutions of environmental problems connected with the processes of wastewater treatment, hydrogen sulfide pollution of various industrial facilities in order to remove such harmful impurities [1, 2]. During their life, people have a multifaceted impact on natural objects, mostly negative [3, 4]. It may be the impact of industry and transport [5], agriculture [6, 7], housing and communal activities [8]. The unpleasant odor that appears in industrial and adjacent waste processing areas is a constant concern for environmental protection and especially for the quality of life [9, 10]. An important problem is also the deterioration of the ecological condition of surface sources of drinking water supply, especially for water bodies, as they are designed to accumulate water reserves [11]. To solve these problems, it is advisable to use selective sorbents-complexites, out of which fiber-based complexites have great advantages [12].

As a result of similar complexing properties of fibers with granular type complexites, they can be considered as a qualitatively new modification. Due to the peculiarities of the polymer chains morphology fibrous complexes have a number of advantages in comparison with granular objects. First of all, it is a high rate of processes with their participation, the availability of reactive groups in polymer chains, and rather high sorption characteristics.

A promising approach to solving the designing and directed synthesis problem of new polyfunctional materials with desired properties based on fibrous complexites is to study the physicochemical characteristics and spatial structure of complexites, which, due to the nature of the groups, usually exhibit the properties of polyelectrolytes. Therefore, the properties of complexites depend on the nature and groups reactivity as well as the polymer matrix [13].

The reactivity of the functional groups of polyelectrolytes is usually researched by studying protolytic equilibria. The material discussed above includes information relating to the catalysts based on granular complexites. The introduction of metal ions into complex-forming polymers results in the creation of materials that differ greatly in properties from the initial reagents [14]. This happens due to the implementation of the coordination bond between the metal ion and the ligand groups of the polymer matrix, leading to the formation of high-molecular complex compounds. The performance characteristics of the materials based on high molecular complex compounds (HMCC) are determined by the type of metal ion introduced into the macromolecule, the nature of the macromolecular chain, and the thermodynamic stability of HMCC [14]. By varying the influence of these factors, it is possible to purposefully synthesize HMCC in order to obtain highly selective catalysts for oxidation processes on their basis.

2 Main Part. Analysis of Literature Data and Problem Statement

Let us give some examples characterizing the catalytic activity of fibrous catalysts as well as modern methods that make it possible to remove H_2S in various ways. Thus, the authors [15] showed that it is impossible to bleach cellulose (wood pulp, paper) with hydrogen peroxide if some traces of heavy metal ions (Fe, Cu, Mn) are found in cellulose fibers. The latter form chelates compounds with the substances present in cellulose, for example, with lignin, and cause the catalytic decomposition of H_2O_2.

Among the many options for removing substance traces that give the air an unpleasant odor, membrane methods or techniques are the preferred options [16]. Their advantages are in the easiness of installation and scalability, selectivity; in addition, the aromatics flows are direct, the automation is achieved with the available operating parameters (pH, temperature, ionic strength), and the operating costs are low. The article [16] presents the process of obtaining membranes from cellulose derivatives containing silver nanoparticles using available raw materials. The technique used for preparing membranes consisted in the reverse phase immersion precipitation of cellulose polymer solutions in methylene-chloride: methanol, volume 2:1. The resulting membranes were morphologically and structurally characterized by scanning electron microscopy (SEM) and high resolution SEM (HR SEM), energy dispersive X-ray analysis (EDAX), Fourier transform infrared spectrometry (FTIR), thermal analysis (TG, A). Then the membranes performance characteristics were determined (extraction efficiency and substance flow) using hydrogen sulfide (H_2S) and ethyl mercaptan (C_2H_5SH) as targets.

The authors [17] studied and developed a method for biotechnological destruction of hydrogen sulfide concentration, which, due to interaction with organic and inorganic compounds, causes great losses in industry. The authors developed efficient sulfide removal by studying sulfate-reducing metabolism and achieved effective elimination of hydrogen sulfide to prevent its negative impact on certain industrial and environmental problems.

So, modern research indicates the relevance of developing methods for the selective removal of hazardous hydrogen sulfide and sulfides. Thus, the authors [18] synthesized a polysulfone (PS) membrane from dimethylacetamide (DMAC) and dimethylformamide (DMF) as a solvent. The presence of hydrogen sulfide in natural gas can result in equipment corrosion, global warming, etc. Thus, the separation of hydrogen sulfide from nitrogen is important. SEM (scanning electron microscopy) images were used to compare the membranes obtained with DMF and DMAC. The authors [18] created an experimental facility and studied the effect of solvents, PS concentration, temperature, and pressure on the separation of H_2S from natural gas. The best results were achieved at 25 °C. The results showed that DMAC solvent was more suitable than DMF, and the degree of selectivity of this type of membrane decreased with the increase in temperature and pressure. M3 membranes (20 % PS, DMAC solvent) were the best membranes.

The research the authors [19] paper contains the analysis of acts of natural and man-made emergency situations related to the deterioration of the water quality occurring in the world and in Ukraine. The method of the express analysis of aqueous solutions which involves measuring the conductivity of the investigated aqueous solutions and calculating the coefficient of identification is proposed. It is shown that the method is informative, simple, fast and environmentally safe.

The authors [20] investigated the H_2S removal efficiency applying four nano-fluids (NF) systems based on deep-penetration eutectic solvent (DES) and measured it carrying out a dynamic absorption experiment. The NF system containing Cu proved to be an excellent absorbent for H_2S removal with significantly improved desulfurization performance compared to the original DES solution. In addition, NF systems have a relatively high regeneration capacity. NF systems and Cu nanoparticles before and after the absorption as well as after the regeneration were characterized according to Fourier transform infrared spectra (FT-IR), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction, transmission electron microscope (TEM) and energy dispersive spectrum (EDS). It was found that ethanolamine, choline cation, and sulfur accumulated on the surface of Cu nanoparticles after absorption, and the solid elements on the surface after regeneration were identified as Cu and S. The S^{2-} ion existed in the form of Cu_2S, and some sulfur was oxidized to zero valence sulfur after regeneration

Environmental pollution is a major problem, and actual recovery methods are limited. The authors [21] investigated a different kind of pollutant removal materials, namely, carbon nanomaterials made from biochar, activated carbon, carbon nanotubes, and graphene to adsorb toxic gases, remove pollutants from ecosystems, and improve anaerobic digestion. Carbon materials have been found to be effective in removing nitric oxide, hydrogen sulfide, heavy metals, dyes, pharmaceutical compounds and other pollutants from the environment with adsorption efficiency up to 80 % and decomposition efficiency up to 99 %. The addition of biochar [21] results in 60% increase in biogas production. Similarly, while composting, ammonia emissions are 60 % less when biochar is added. Biomass-based carbon materials appear to be economical, sustainable and environmentally friendly. The authors [22] the method for rapid detection of hazardous pollution of the atmosphere of cities, which is based on dynamic measures of recurrence (repeatability) of the states of the pollution concentration vector, was developed. The new scientific result is related to the use of the unconventional modification of the known measures of recurrence based on the dynamic window averaging the current recurrence of the states of atmospheric pollution concentration.

Taking into account the above mentioned studies and factors, fibrous structures – fibers of natural and synthetic origin – can be an effective and convenient matrix for HMCC used as catalysts. Such data in literature are very limited.

3 The Purpose and Objectives of the Study

The purpose of this work is to study the catalytic activity of Cu^{2+}, Co^{2+}, and Ni^{2+} HMCC with complexing CG and NAG fibers containing carboxyl (NAG), amidoxime, and hydroxam groups, using the decomposition reaction of hydrogen peroxide and oxidation reaction of sulfur compounds (H_2S, Na_2S) as an example.

4 Materials and Research Methods

4.1 Materials

Samples of fibrous complexite CG were used as objects of study. The fiber is a copolymer of cellulose and polyacrylonitrile with hydroxamic acid and amidoxime groups. The nature of the reaction centers, physicochemical properties - ion-exchange, solvation, protolytic complexite CG are given in [23]. Complexite NAG was received by chemical modification of the industrial fiber nitron; its matrix contains functional groups of hydroxamic acid, amidoxime, and a small percentage of carboxyl groups. The polymer belongs to polyampholytes. The starting form of a polymer used in the experiments is mixed (hydrogen-hydrate-salt, H/OH, Cl): hydrogen by carboxylic, hydroxamic, oxyimino groups of amidoxime, and hydrogen-hydrate-salt – by amidoxime. Total exchange capacity, mmol/g of the complexite was calculated from solutions of 0.1 M NaOH и 0.1 M HCl in water. Physico-chemical properties, ion exchange, solvation, protolithic, of the complexite NAG are described in [23].

Weighed portions of metal salts were selected in such a way that the number of metal ions in them corresponded to their content in HMCC [23, 24]. Simultaneously, for comparison, some studies were carried out in the absence of a catalyst. The rate of the process was controlled using the volumetric method [23], and the concentration of H_2O_2 was controlled using the permanganatometry method [23]. Kinetic curves VO_2 - τ (V is the volume of released oxygen in ml, τ is the process time in minutes) were studied at: constant catalyst weight (0.1 g), changing the initial concentration of H_2O_2 (0.06-0.3 mol/l); a constant concentration of H_2O_2 (0.3 mol/l) and various weighed portions of the catalyst (0.01-0.1 g); constant concentrations of H_2O_2 (0.3 mol/l), catalyst weights (0.1 g) and different pH values (from 5.5 to 12.5) created by adding NaOH solution (with the concentration of 0.5 mol/l). The discrepancies between the results of 2-3 simultaneous experiments did not exceed 3-4%.

4.2 The study results of kinetic research

The rate of the process was determined according to the linear segments of the kinetic curves, and according to the dependence of the decomposition rate on the concentration of H_2O_2 (in logarithmic coordinates), the weight portion of the catalyst, and the pH of the medium, the order of the reaction was found with respect to H_2O_2, the catalyst, and the concentration of protons in the system. Similar research was carried out for the oxidation of H_2S and Na_2S compounds.

With the preliminary goal of selecting concentrations during the oxidation process, we carried out kinetic studies of H_2O_2 decomposition in the presence of HMCC. And only then some model experiments were carried out to purify gas mixtures from hydrogen sulfide.

5. Discussion of the Study Results of the Kinetic Activity of Complexite

5.1 Study of catalytic activity

The kinetic curves of gas emission indicate that the rate (W) of the decomposition reaction in the presence of HMCC and low molecular weight complex compounds (LMCC) increases with the rise in H_2O_2 concentration, the addition of a catalyst, while the order of the reaction with respect to peroxide and catalyst is equal to one. With an increase in pH, the rate increases, reaching a maximum value at pH 8.5, then decreases and increases again from pH 9.5 to 12.5. In the pH ranges of 5.5–8.5 and 9.5–12.5, an inverse dependence of W on the proton concentration in the system is observed. The reaction order n with respect to $[H^+]$ decreases from 0.3 (pH 5.5–8.5) to 0.1 (pH 9.5–12.5), and in the pH range 8.5–9.5 it acquires negative values. The data obtained are presented in Table 1.

Metal salts catalyze the decomposition reaction weaker than the corresponding LMCC [15]. The established experimental facts allow us to assume that the catalytic effect in the HMCC – H_2O_2 systems is achieved due to the formation of certain coordination compounds by metal ions in the complexite phase. The complex nature of the dependences of the reaction rate on pH can be explained taking into account the distribution of Cu^{2+}, Co^{2+}, Ni^{2+} not only over the complex forms of the M – L type (where M is a metal ion, L is a functional group of the complexite), but also according to the forms of mixed hydroxo-, peroxomonomeric and dimerized complexes. To prove this, we obtained the IR spectra of the complexite and all HMCs, which resemble each other in appearance, but there is some difference in certain vibration frequencies.

Table 1. Catalytic activity of HMCC in the decomposition reaction of H_2O_2 with the content of metal ions in CG - Cu^{2+} = 0.5 mmol/g, Co^{2+}, Ni^{2+} = 0.4 mmol/g, in NAG - Cu^{2+} = 0.6 mmol/g, Co^{2+}, Ni^{2+} = 0.5 mmol/g

HMCC	$W \cdot 10^4$ [mol/(L·s·g)]			$k \cdot 10^1$ [L/(mol·c)]			lg K_{ins}
	[pH]			[pH]			
	6.3	8.5	12.2	6.3	8.5	12.2	
Without catalyst	0.22	0.45	0.58	-	-	-	
CG - Cu	1.19	3.27	7.22	14.9	24.4	73.6	7.8
CG - Co	0.89	2.68	0.67	2.62	4.45	-	6.8
CG - Ni	0.61	1.49	1.79	1.78	2.62	8.99	6.6
NAG - Cu	2.52	3.83	5.63	21.4	23.6	41.6	7.7
NAG - Co	2.43	3.12	2.14	4.56	6.32	-	6.9
NAG - Ni	1.93	2.94	2.95	3.58	5.33	9.45	6.6

The IR spectrum of the complexite has absorption bands at the level of 3600 - 3200 and 2920 cm^{-1}, which characterize the tensile vibrations of the NH and OH groups in hydroxamic acids. The absorption in the range of 1680 and 1650 cm^{-1} is connected with the tensile vibrations of the C = O, NH_2, and C = N bonds and is characteristic of monosubstituted amides. The band at 900 - 890 cm^{-1} is specific for hydroxamic acids, which is connected with tensile vibrations in the NO bond. The absorption intensity at 1550 cm^{-1} depends on the pH medium. In an alkaline medium, it increases, and in an acidic medium it decreases, regardless of the solvent composition. At the same time, in an acid medium, the 1680 - 1650 cm^{-1} band expands to the high-frequency region, and the shoulder appears at 1760 cm^{-1}. This is due to an increase in the concentration of dissociating hydroxamic groups in an alkaline medium and an increase in the protonation degree of amidoxime groups, accompanied by complex formation of cations, the deformation vibrations of which are found in the range of 1760 - 1750 cm^{-1}. Such changes are characteristic of the complexing formation of hydroxamic acids and indicate the coordination of copper(II), cobalt(II), and nickel(II) ions with the hydroxamic groups of the complexite [14].

5.2 The ability of reducing the concentration of hydrogen sulfide in the presence of complexites

Experimental data on the decrease in the concentration of hydrogen sulfide in the presence of complexites are presented in Table 2.

The scarcity of data about the influence of the pH environment on the composition of the coordination centers of the above mentioned fibrous catalysts and on the ratio of different complex forms of metal ions in the substrate makes it impossible to suggest a catalysis mechanism for the decomposition of H_2S, H_2O_2 in the studied systems. For the same reasons, it is difficult to estimate the rates of the reaction stages involving protonated and deprotonated forms of complexites, with the participation of HMCC and complex forms of metal ions in solution, as a result of which it is impossible to carry out a correct kinetic analysis of the processes.

According to our studies (Tables 1 and 2), the rate of H_2O_2 decomposition increases in the series Ni<Co<Cu. There are slight differences in the activity of identical HMCC with CG and NAG complexites. This may be due to the presence in the NAG matrix of a wider range of functional groups involved in the catalytic process, as well as due to the differences in the solvation characteristics of complexites [24]. A significant decrease in the activity of cobalt HMCC (pH 12.2) is probably due to some change in the redox potential of these complexes.

Table 2. Purification of gas mixtures from hydrogen sulfide using fibrous complexites

H_2S, [%] in gas mixture	HMCC	Catalyst, [g]	Metal in fiber, [mg-equ/L]	Alkali concentration [mol/L]	Temperature, [°C]	Gas velocity, [ml/min]	Flow time, [min]	Purification rate [%]
1.0	NAG-Ni	0.05	1.0	0.05	40	20	60	100
5.0	CG-Cu	0.05	1.8	0.05	40	20	60	100
10.0	NAG-Cu	0.10	2.0	0.10	30	10	45	100
10.0	CG- Ni	0.10	16.2	0.10	30	10	45	99
20.0	NAG-Cu	0.15	3.0	0.15	20	5	30	100
20.0	CG- Ni	0.15	22.5	0.15	20	20	30	95

Thus, the experimental studies performed indicate that the catalytic activity of HMCC in the decomposition reaction of H_2O_2 depends on pH, exceeds the activity of model low molecular weight complex compounds [23], and rises with the increase in the stability constants of polymer complexes (Table 1).

The introduction of metal ions into complex fibers as a result of some coordinated bond formation between the metal and polymer ligand groups produces high-molecular complex compounds. The performance and selective properties of materials based on HMCC can be determined by the metal ion type introduced into macromolecules, the nature of the polymer chain, and thermodynamic stability. By changing the effect of the above mentioned factors, HMCC can be synthesized to be used as highly selective catalysts for various chemical processes.

In conclusion, we should note that the actual experimental material already available and the research intensification in the direction of a detailed study of the factors determining the structure and properties of fiber-based HMCC will help to understand the nature of the catalytic action by determining the role of metal and polymer. This can significantly expand the range of catalysts activity and help predict the processes in which they will be catalytically active.

6 Conclusions

The paper presents some data on the catalytic activity of high-molecular complex compounds with Cu^{2+}, Co^{2+}, Ni^{2+} ions with complex-forming fibers containing carboxyl, amidoxime, hydroxamic groups, using the example of hydrogen peroxide decomposition reaction and oxidation reaction of H_2S, Na_2S compounds.

An inhibitory effect on the oxidation process of the fiber functional groups in the range of pH 5.5 - 12.5 was revealed.

It has been established that the catalytic activity of complexites depends on pH, the stereochemistry of the coordination centers in the fiber matrix and significantly exceeds the activity of model low molecular weight complex compounds. As the stability constants of complexites increase, their activity increases as well.

References

[1] Rybalova O., Artemiev S., Sarapina M., Tsymbal B., Bakhareva A., Shestopalov O., Filenko O. Development of methods for estimating the environmental risk of degradation of the surface water state. Eastern-European Journal of Enterprise Technologies, **2 (10–92)** (2018) 4–17.

[2] Loboichenko V., Vasyukov A., Tishakova T. Investigations of Mineralization of Water Bodies on the Example of River Waters of Ukraine. Asian Journal of Water, Environment and Pollution. **14 (4)** (2017) 37–41.

[3] Bezsonnyi V., Tretyakov O., Khalmuradov B., Ponomarenko R. Examining the dynamics and modeling of oxygen regime of chervonooskil water reservoir. Eastern-European Journal of Enterprise Technologies, **5 (10–89)** (2017) 32–38.

[4] Popov O., Iatsyshyn A., Kovach V., Artemchuk V., Taraduda D., Sobyna V., Sokolov D., Dement M., Hurkovskyi V., Nikolaiev K., Yatsyshyn T., Dimitriieva D. Physical features of pollutants spread in the air during the emergency at NPPs. Nuclear and Radiation Safety. 2019. Vol. 4, No. 84, (2019) 11.

[5] Pospelov B., Rybka E., Togobytska V., Meleshchenko R., Danchenko Y., Butenko T., Volkov I., Gafurov O. Yevsieiev V. Construction of the method for semi-adaptive threshold scaling transformation when computing recurrent plots. Eastern-European Journal of Enterprise Technologies, **4 (10–100)** (2019) 22–29.

[6] Danchenko Y., Andronov V., Kariev A., Lebedev V., Rybka E., Meleshchenko R., Yavorska D. Research into surface properties of disperse fillers based on plant raw materials. Eastern-European Journal of Enterprise Technologies, **5 (12–89)** (2017) 20–26.

[7] Loboichenko V., Strelets V., Leonova N., Malko A., Llyinskiy O. Comparative analysis of anthropogenic impact on surface waters in Kharkiv region. Indian Journal of Environmental Protection, **40 (2)** (2020) 134–139.

[8] Vasenko A., Rybalova O., Kozlovskaya O. A study of significant factors affecting the quality of water in the Oskil River (Ukraine). Eastern-European Journal of Enterprise Technologies, **3 (10–81)** (2016) 48–55.

[9] Pospelov B., Andronov V., Rybka E., Krainiukov O., Maksymenko N., Meleshchenko R., Bezuhla Y., Hrachova I., Nesterenko R., Shumilova A. Mathematical model of determining a risk to the human health along with the detection of hazardous states of urban atmosphere pollution based on measuring the current concentrations of pollutants. Eastern-European Journal of Enterprise Technologies, **4 (10)** (2020) 37–44.

[10] Loboichenko, V., Leonova, N., Shevchenko, R., Kapustnik, A., Yeremenko, S., Pruskyi, A. Assessment of the impact of natural and anthropogenic factors on the state of water objects in urbanized and non-urbanized areas in lozova district (Ukraine). Ecological Engineering and Environmental Technology, **22 (2)** (2021) 59-66.

[11] Loboichenko V., Andronov V., Strelec V. Evaluation of the metrological characteristics of Natural and treated waters with stable salt composition identification method. Indian Journal of Environmental Protection, **38 (9)** (2018) 724–732.

[12] N. Korovnikova, A. Dubyna, V. Oliinik Features of complex formation of a fibrous complexite with nickel ions in water–dioxane mixtures. Eastern-European journal of enterprise technologies organic and inorganic substances, **2** (2019) 6 15–22.

[13] N. Korovnikova, A. Dubyna Research into complexing properties of polyacrylonitrile complexite in the mixtures of water-dioxane. Eastern-European Journal of Enterprise Technologes, **89** (2017) 63–69.

[14] L.V. Miroshnik, N. I. Korovnikova, Y.V. Shabadash Stability of copper(II) complexes with cellulose complexite in water-dioxane mixtures. Russian Journal of Inorganic Chemistry, **51** (2006) 4 649–655.

[15] L.V. Miroshnik, N.I. Korovnikova Catalytic action of a modified polyacrylonitrile fibres III International Conf. "Electronic processes in organic materials" (2001) 156-157.

[16] A. Nechifor, C. Cotorcea, Removing of the Sulfur Compounds by Impregnated Polypropylene Fibers with Silver Nanoparticles-Cellulose Derivatives for Air Odor Correction. Membranes, **11** (2021) 4 256.

[17] D. Dordević, S. Jančíková, I. Kushkevych Hydrogen sulfide toxicity in the gut environment: Meta-analysis of sulfate-reducing and lactic acid bacteria in inflammatory processes. Journal of Advanced Research, **27** (2021) 1 55-69.

[18] A. Shokri Synthesize and characterization of polysulfone membrane for the separation of hydrogen sulfide from natural gas. Surfaces and Interfaces, **8** (2021) 101.

[19] Loboichenko V., Strelec V. The natural waters and aqueous solutions express-identification as element of determination of possible emergency situation. Water and Energy International, **61 (9)** (2018) 43–50.

[20] Liu X., Wang B., Li M. Enhanced removal of hydrogen sulfide using novel nanofluid system composed of deep eutectic solvent and Cu nanoparticles. Journal of Hazardous Materials, **405** (2021) 5 124-127.

[21] K. Gopinath, D. Prakash (Environmental applications of carbon-based materials: a review. Environmental Chemistry Letters volume, **1** (2021) 9 557–582.

[22] Pospelov B., Rybka E., Meleshchenko R., Borodych P., Gornostal S. Development of the method for rapid detection of hazardous atmospheric pollution of cities with the help of recurrence measures. Eastern-European Journal of Enterprise Technologies, **1 (10–97)** (2019) 29–35.

[23] N. Korovnikova, A. Dubyna Research into complexing properties of polyacrylonitrile complexite in the mixtures of water-dioxane. Eastern-European Journal of Enterprise Technologes, **89** (2017) 63-69.

[24] N. Korovnikova, A. Dubyna, V. Oliinik Chemical cellulose-based fibers of decreased flammability Eastern-European journal of enterprise technologies. technology organic and inorganic substances, **2** (2020) 5/6 33-39.

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Adsorption Purification of Wastewater from Chrome Ions and Phosphate Ions with Bentonite

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Keywords: ecological safety, natural clay sorbents, adsorption, bentonite, ions of heavy metals, modification.

Abstract. The work is devoted to solving the current problem of increasing the level of environmental safety of treatment industrial wastewater of leather production from chromium ions (III) through the use of natural and modified bentonite. The investigation about the efficiency of purification of model solutions, which contain 1 g/dm^3 of chromium ions and 0.75 g/dm^3 of phosphate ions was carried out by the method of ideal displacement. In our research, we proposed a method of sequential adsorption, according to which phosphate ions are absorbed in the first stage and chromium ions are sequentially adsorbed in the second stage. Structural features of natural carbonate-rich and modified with chromium and phosphate ions bentonite clay have been studied, researched and analyzed.

Introduction

In addition to activated carbon and synthetic ion exchangers, natural clay sorbents are becoming increasingly important. which are affordable, low cost and provide effective wastewater purification from ammonium ions, heavy metals, non-polar organic products [1, 2]. As a rule, such sorbents are unprofitable to regenerate due to their low cost. Waste sorbents are often stored on the territory of enterprise, often without authorization. Therefore, the issues of maximum utilization of sorption capacity of sorbents and ways of their effective utilization remain relevant.

Waste bentonite can be regenerated by desorption. However, the cost of natural clay sorbents is low, so it is inappropriate to plan the regeneration of waste sorbents, as the cost of regeneration will be higher than the cost of new sorbents. In this case, there is another perspective direction of waste bentonite use - its application in sequential sorption.

The purpose of the work was to research the efficiency of waste water purification from chromium ions (III) by natural clay sorbent bentonite, for neutralization of harmful substances in waste water of technological processes of galvanic production. The possibility and modes of application of bentonite modified with phosphate ions for wastewater purification from heavy metal ions have been established in order to increase resource conservation and environmental friendliness of water purification technologies.

Materials and Methods

The possibility of using the adsorbent twice in successive water purification processes was determined by a comparative study of the degree of adsorption of natural bentonite and bentonite, pre-saturated with pollutant ions.

To determine the effect of time (between 30 and 930 minutes) on the efficiency of chromium ion extraction (III) from solution with the concentration $C(Cr^{3+})$ = 1g/l 2 units with the addition of 20 g of adsorbent were put (bentonite clay of natural origin and bentonite clay saturated with phosphate ions), meanwhile the research was carried on [3].

The results of the iodometric titration method are presented in table 3.1. (the amount of sodium thiosulfate spent on of the sample titration). The absorption of the solution through the sorbent was attempted at a constant speed of 3-4 min / ml.

The effective volume (Veff) was used to simplify the calculations and the visual image as a dimensionless quantity, calculated by the formula:

$$V_{eff} = \frac{V_{solution}}{V_{column}} \quad (1)$$

The time of selection was determined every 10 ml of the solution, control points were determined every 50 ml of the solution, which were V_{eff} =1,03 i 1,37 with a mass of sorbent 20g. The research results are presented in Fig. 1.

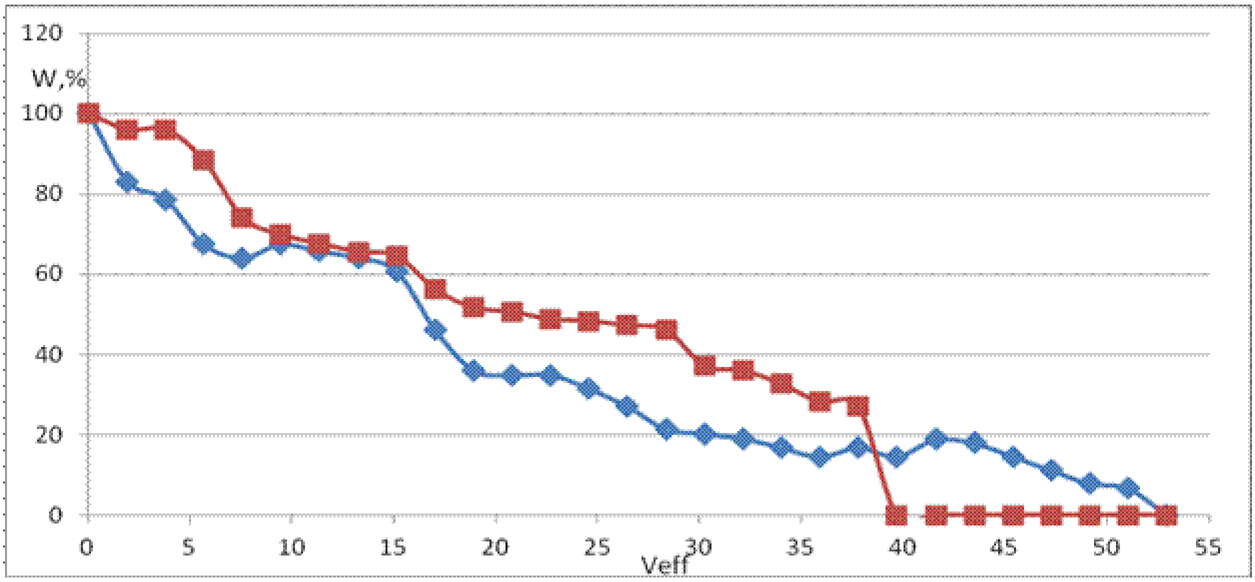

Fig. 1. Effect of volume solution on the efficiency of chromium ions absorption by bentonite: —♦— pure bentonite;—■— bentonite saturated with phosphate ions

In general, adsorption corresponds to the general laws of using natural clays as adsorbents for wastewater purification from heavy ionic metals by the method of ideal displacement, namely during the first time intervals we observe maximum absorption of pollutant, and then absorption decreases.

It is unusual that when using waste bentonite, the first traces of the contaminant appear immediately in a significant amount, which may be due to the pre-fixation of the active centers of the sorbent by other cations and anions. We can claim that in each case the adsorption with a fixed layer of sorbent is gradual and has a uniformly cumulative nature [4].

Pre-saturation of the adsorbent with heavy ionic metal has almost no effect on the adsorption efficiency of phosphate ions depending on the volume of pumped model solutions (Fig. 2). However, the presence of chromium ions traces (III) in the test solution after desorption was determined by qualitative analysis, which indicates a certain erosion of the soluble compounds formed by the acid solution, and pre-surface saturation of the adsorbent with heavy ionic metal makes the process of chemisorption more difficult.

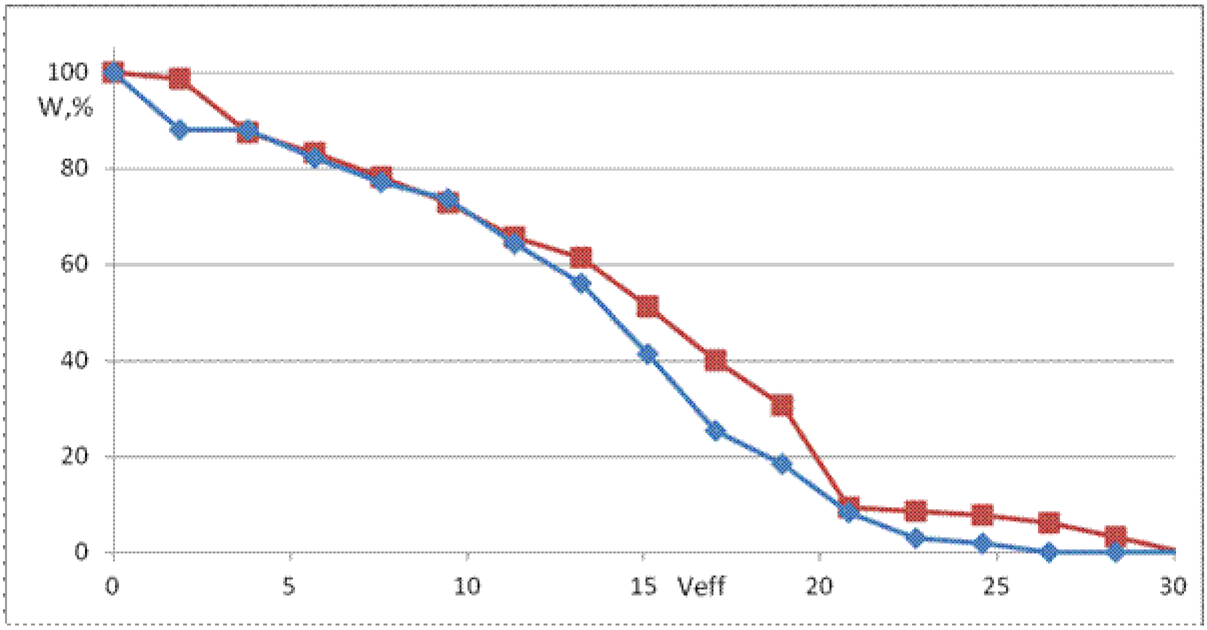

Fig. 2. Effect of volume solution on the efficiency of PO_4^{3-} bentonite absorption:
—♦— pure bentonite;—■— bentonite saturated with chromium ions

According to the results of the experiment generalized sorption rates are presented in Fig. 1 and Fig. 2.

According to the results of the experiment, the maximum absorption of chromium (III) ions at the expense of sorbent weighing 20 g is 95.95% in the case of natural bentonite, and in the case of waste bentonite is 83.14% (Table 1).

Table 1. Generalized indicators of sorption efficiency of Cr^{3+} ions according to different bentonite characteristics

№	Bentonite characteristic	Saturation time (*t*), [min].	Effective volume (V), [ml]	General volume ($V_з$), [ml]	Dynamic of exchange capacity (T)	α, %	
						α_{ef}	$\bar{a}$
1	Natural bentonite	630	500	1000	0,025	95,95	53,94
2	$(PO_4)^{3-}$ – bentonite	930	500	1400	0,024	83,14	52,04

However, clay saturated with phosphate ions gave bigger absorption capacity and yield time of 10 ml of sample, which can be explained by better development of the active sorption surface. The average pollutant absorption values ($\bar{a}$) were almost the same. Thus, the previous use of bentonite at the stage of removal from phosphate ions from polluted water has almost no effect on the degree of absorption of chromium ions, but the purification time of a solution of a certain volume is reduced and significantly increases the volume of pumped effluent (in 40%).

Table 2. Generalized indicators of PO_4^{3-} ions sorption efficiency with different bentonite characteristics

№	Bentonite characteristic	Saturation time (*t*),[min]	Effective volume (V), [ml]	Dynamic of exchange capacity (T)	α,%	
					α_{ef}	$\bar{a}$
1	Natural bentonite	480	800	0,019	98,78	53,68
2	Cr^{+3} – bentonite	400	700	0,013	88,20	51,98

The results presented in Table 2 indicate that the previous use of bentonite at the stage of chromium ions removal from polluted water has a slightly negative effect on the degree of phosphate ions absorption, cleaning efficiency decreases slightly and reduces the volume of pumped effluent by 12.5%. Thus, the use of waste bentonite at the stage of wastewater purification from heavy ionic metal is impractical for wastewater purification from phosphate ions.

To determine the efficiency of sequential adsorption, as well as to predict the main methods and directions waste sorbents use, it is necessary to have reliable instrumental methods for studying the structure of clay minerals, for which the X-ray phase method was used.

X-ray phase analysis was carried on an X-ray diffractometer "DRON-2" in monochromatized Co-Kα radiation (λ = 1,7902A). The identification of compounds (phases) was carried on by comparing the interplanar distances (d, A) and relative intensity (I () = I / I0) with the experimental curve according to the electronic file PCPDFWIN. The research results are presented in Fig. 3.

The data of X-ray phase analysis correspond to the natural bentonite clay of the Cherkasy deposit of the second layer (sample 1). X-ray lines are quite blurred in all samples, which is typical for most natural clays of predominantly amorphous composition. The main difference of this clay is the presence of paligorskite, and the composition of natural clay is represented mainly by montmorillonite, hydromica and kaolinite. Montmorillonite and kaolinite are the main minerals of the pellet fraction (60-65%) [5].

In the available diffractograms, the position of the main peaks of the SiO_2 crystalbolite can be considered as a marker that characterizes the deep transformations of the clay structure. [3]. n the natural sample of bentonite (sample 1), the main peaks of SiO_2-quartz are located at the temperature rates 26°, 30 ° and 48 °. On diffractograms 2-4, which characterize the waste samples of bentonite, we do not observe a significant shift of the peaks to lower values of diffraction angles, also very similar to the intensity of X-ray lines. The content of SiO_2 crystalbolite in all samples ranges from 10% to 20%. Therefore, we can say that adsorption processes occur mainly on the surface of bentonite.

On diffractograms 2-4 we have a number of peaks of different modifications of Cr_3O_4. In sample 2: bentonite saturated with chromium ions, the content of modifications with chromium ions up to 3%, in terms of Cr_2O_3. For sample 3: bentonite, successively saturated with chromium ions and phosphate ions, only traces of Cr_2O_3 were recorded, and in sample 4: bentonite, successively saturated with phosphate ions and chromium ions, the content of modifications with chromium ions is 3-4%. The data are confirmed by the results of analytical studies of the content of chromium ions in bentonite - sample 4 is characterized by the highest absorption of chromium ions. Therefore, pre-acid modification increases the degree of absorption of chromium ions. In the case of successive absorption of phosphate ions by bentonite and then chromium ions (sample 3), it is most likely that chromium ions are washed out of the clay structure when passed through a column of phosphate solution. This assumption was confirmed by qualitative analysis - traces of chromium ions in the purified solution were identified.

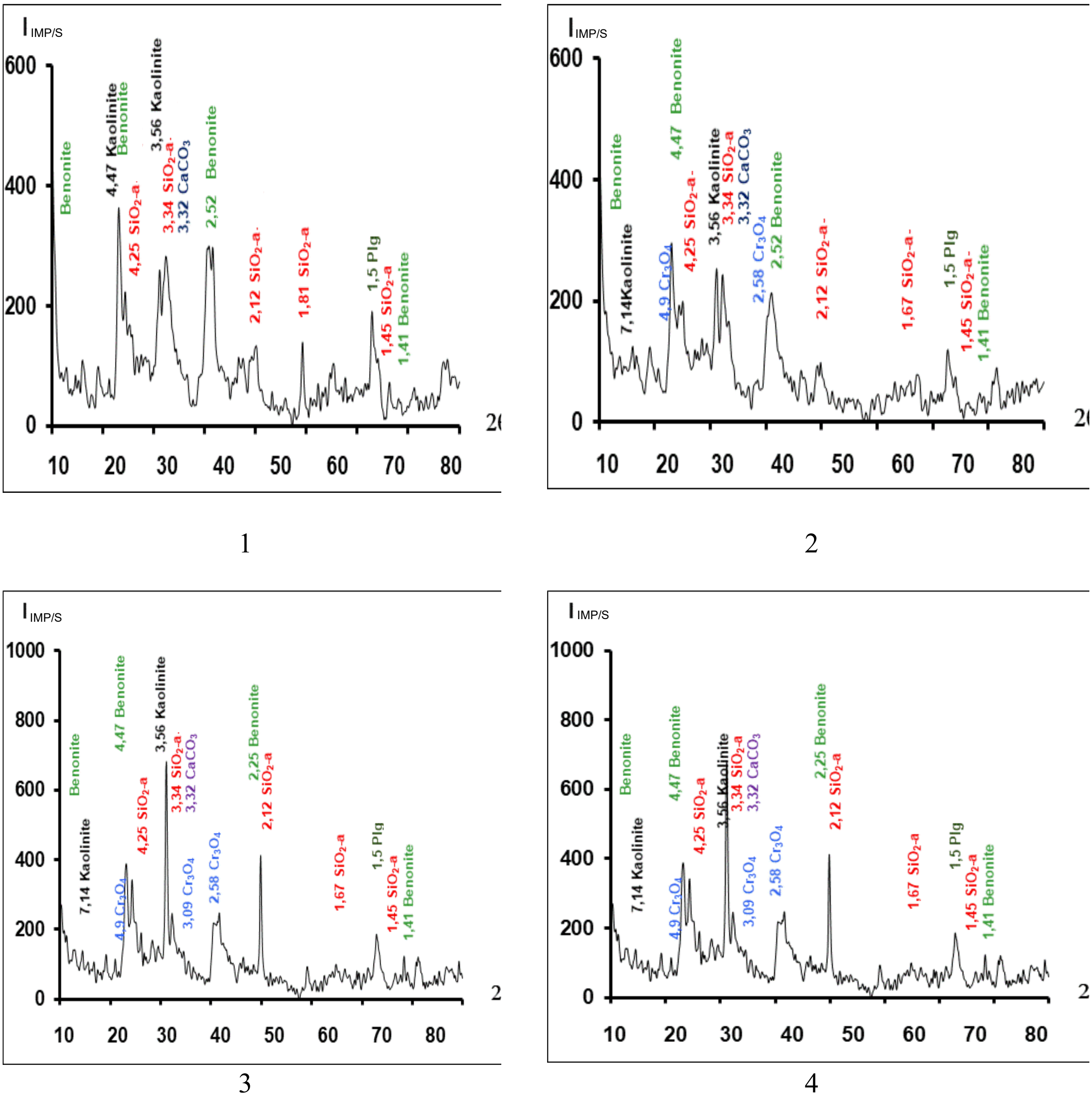

Fig. 3. Diffractograms of bentonite samples

On diffractograms 2-4 we observe a significant deterioration of the diffraction pattern under temperature rates 34°-42°, as well as the decrease in the content of calcite. Moreover, the most similar diffractograms in this area for samples 3 and 4. Probably, in the waste products we have a higher content of dispersed and colloidal oxides, which prevents the manifestation of the corresponding reflexes on the diffractograms. The absorption of acid residues promotes dispersion and increases the amorphous structure. This is a positive fact in the possible use of waste bentonite for filling polymer structures, because the fillers montmorillonites in a dispersed state [6].

Conclusion

In order to make full use of the sorbent absorption capacity, the method of adsorption of Cr^{3+} ions by passing wastewater through a layer of bentonite previously saturated with phosphate ions was chosen. It is recommended to reuse waste dried sorbent for wastewater purification containing heavy ionic metal. The method can be used in the process of water treatment of industries that contain excessive amounts of chromium ions, it provides not only efficient wastewater purification, but also the rational use of adsorption material.

X-ray phase studies confirmed the absence of significant structural changes in the adsorbent due to the chromium ions absorption and phosphate ions. Data of X-ray phase analysis by the results of analytical studies of chromium ions in bentonite - a sample consistently saturated with PO_4^{3-} and Cr^{3+} ions is characterized by the highest content of chromium ions acid modification of bentonite clay leads to destruction of carbonate component.

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References

[1] M. Malovanyy, K. Petrushka, I. Petrushka, Improvement of Adsorption-Ion-Exchange Processes for Waste and Mine Water Purification. Chemistry & Chemical Technology, **13(3)** (2019) 372–376.

[2] M. Malovanyy, H. Sakalova, T. Vasylinycz, O. Palamarchuk, J. Semchuk, Treatment of Effluents from Ions of Heavy Metals as Display of Environmentally Responsible Activity of Modern Businessman. Journal of Ecological Engineering, **20(4)** (2019) 167–176.

[3] Ch. Soloviy, M. Malovanyy, O. Palamarchuk, I. Trach, H. Petruk, H. Sakalova, T. Vasylinych, N. Vronska. Adsorption method of purification of stocks from chromium (III) ions by bentonite clays. Journal of water and land development, **48(I–III)** (2021) 99–104.

[4] M. Malovanyy, O. Blazhko, H. Sakalova, T. Vasylinych, Ecological Aspects of Clay Sorption Materials Usage in Leather and Fur Production Technologies. Materials Science Forum, **1038** (2021) 276-281.

[5] O.V. Kyrychenko, Mineralogical composition and thermal transformation natural and iron – modified bentonite clays. Naukovyy visnyk NLTU Ukrayiny, **20.3** (2010) 77-82.

[6] O. Mokrousova, The organo-mineral composition for retaining – filling of leather semi-fin semi-finished item, 3rd International Conference on Advanced Materials and Systems. (2010) 85-90.

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The Use of Date Palm Fronds Waste as Biomass in Saudi Arabia, Madina Region Case Study

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Keywords: Biomass, palm waste, power generation, environment, alternative power sources.

Abstract: Even though dates are produced in large scales in Saudi Arabia, it is not the only product palm can offer. Transformative products of palm that can be beneficial for the community are intense. For instance, using fronds waste as a biomass to generate power at remote areas or central cities where the palm population is intense might be a transformative product of palm. Using natural waste as a supplement source of electricity at the communities living near palm farms will have a profound effect on the environment and economy. This paper discusses the feasibility of using palm fronds as a biomass in Saudi Arabia. It complies with the kingdom's strategic power plan where alternative power sources are encouraged in the vision 2030. This paper briefly illustrates the opportunity of using biomass, statistics of palm in Saudi and the use of biomass as a feedstock to generate electricity in the Madina region as a case study.

Introduction

Agricultural waste is considered in the literature for the production of different byproducts [1]. Using biomass as a renewable energy source for power generation is one of the practical implementations. The advanced technology used in the biomass-to-power plants results in fewer emissions in the plant site. This adds to the benefit of using agricultural waste as biomass where carbon emission will be reduced efficiently.

The demand for electricity in Saudi Arabia is rising. According to Saudi Arabia's Renewable Energy Strategy and Solar Energy Deployment Roadmap report made by KACARE, the power demand would almost triple in the next 20 years. The report shows a 60 GW difference between the existing capacity and the peak future demand. It suggests a target of 52 GW power produced by renewable energy sources with 3 GW produced from waste to energy sources. This will considerably reduce the greenhouse gas emissions in Saudi Arabia that was 580 M ton in the year 2019 [2].

Saudi Arabia is the second largest date producer in the world with 28.5 million palm as 2018 data of the Saudi General Authority for Statistics [3]. Palm farms are distributed across Saudi Arabia. However, most of the palm populations are concentrated in Riyadh, Qasim, Madina and eastern regions as presented in Fig. 1. Usually a palm produces an average waste of 13 fronds per year [4]. This results in thousands of tons of dry fronds trimmed away and thrown or even burned at the farm site [5]. With no agricultural waste landfills and proper treatment of the waste, the environmental effect is huge. We propose using the fronds waste as a biomass to generate power in remote areas or central cities where the palm population is intense. Using natural waste as a main or supplement source of electricity at the communities living near palm farms will have a profound effect on the environment and economy. However, this is hindered by the difficulty of collecting the waste in the first hand.

Waste collection and supply chain management, shipping and storing are important considerations for the successful implementation of the agriculture waste power plant. However, securing enough biomass for the proper operation of the plant in Saudi Arabia is difficult due to the following reasons. First, farms in the kingdom, mostly small to medium sizes, are scattered away in regions where the palm population is intense. In the Madina region for instance, palm farms are separated across a radius of 250 km from the city of Madina as shown in Fig. 2. Second, the cleaning season varies based on weather and customs. This requires arrangements and communication protocols with the farm's owners. Finally, fronds usually occupy large space due to their bushy leaves and irregular shapes. This will affect the shipping efficiency where most of the container's space would not be utilized.

In this study, a comprehensive solution has been proposed where the waste collection and supply chain management are both used properly for the successful collection of the palm waste. This solution can be applied by using automated machines and optimized supply chain practices to maximize the waste collection quantities during the cleaning season. We will analyze the cost of waste collection based on a storage location in Al Madina city.

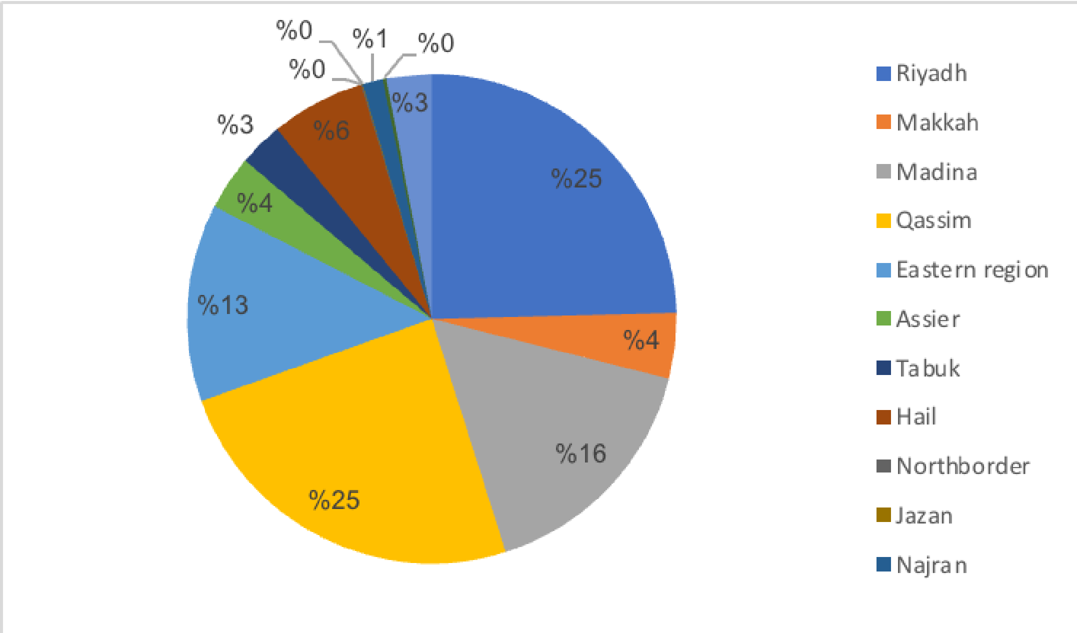

Figure 1: Intensity of palms in Saudi Arabia, https://www.stats.gov.sa/ar/22

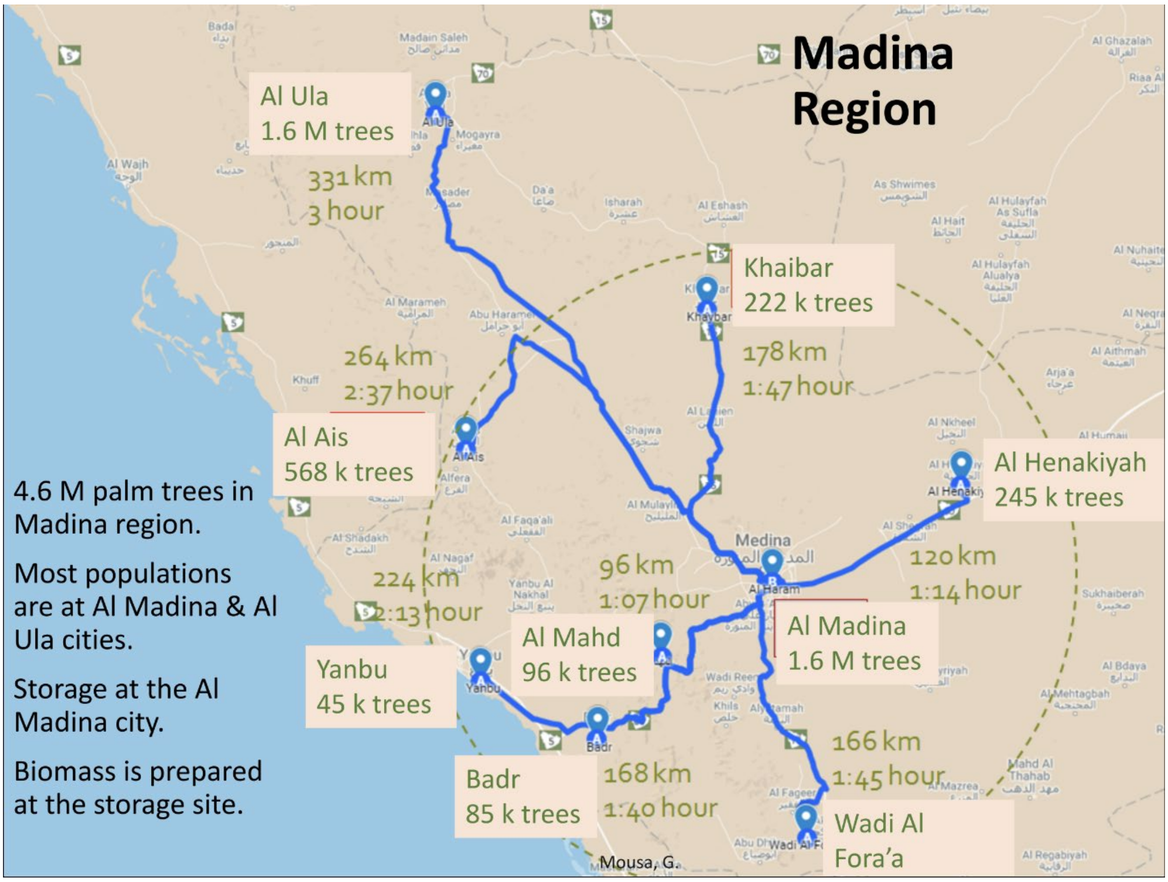

Figure 2: Distribution of palm farms in the Madina region, https://www.stats.gov.sa/ar/22

Collection Process

Biomass made of palm waste can benefit the environment first by avoiding waste being burned, and second by reducing the use of fossil fuel or natural gas for power generation. However, reduction of fronds' space occupation during transportation must be implemented to secure enough quantities of biomass. This can be done by cutting off the fronds' tails and tops, and trimming away leaflets. Cutting off the frond's tail and top will result in straighter shapes that are easier to deal with. Trimming away leaves will result in separated leaflets and stalks. This will give better space management during transportation, and allow mixing different palm waste materials while preparing the biomass. Applying such a process on fronds manually consumes time. This was validated by collecting the waste of a small size palm farm in Al Madina city. It took 5 business days and 6 workers to process 4000 fronds on a farm site. Stalks only were shipped to Jeddah in a single trailer that usually can accommodate only 400 fronds in a conventional way as shown in Fig. 3. The total cost of processing and shipping combined was 1 SAR per stalk.

Figure 3: Conventional and non conventional transportation of waste palm fronds

Using automation instead of manual labor would increase the quantities of waste collection. The automation system would need to collect 20 fronds per minute to finalize the waste of a small palm farm with 700 palms in a single day shift. This is equivalent to 9600 fronds per shift. The process will take place at the farm site as shown conceptually in Fig. 4. The automation system contains a set of machines that finalize processing the fronds, and store stalks and leaflets in separate containers in preparation for shipping to the storage area. Such a system does not exist in the market as far as we know. At the storage, fronds will be dried, shredded and fabricated to biomass. It is important to mention that shredding fronds at the farm site is not recommended where fronds might not be fully dry. Having moisture at the fronds might affect the heating capacity of the biomass, and hence reduce its quality.

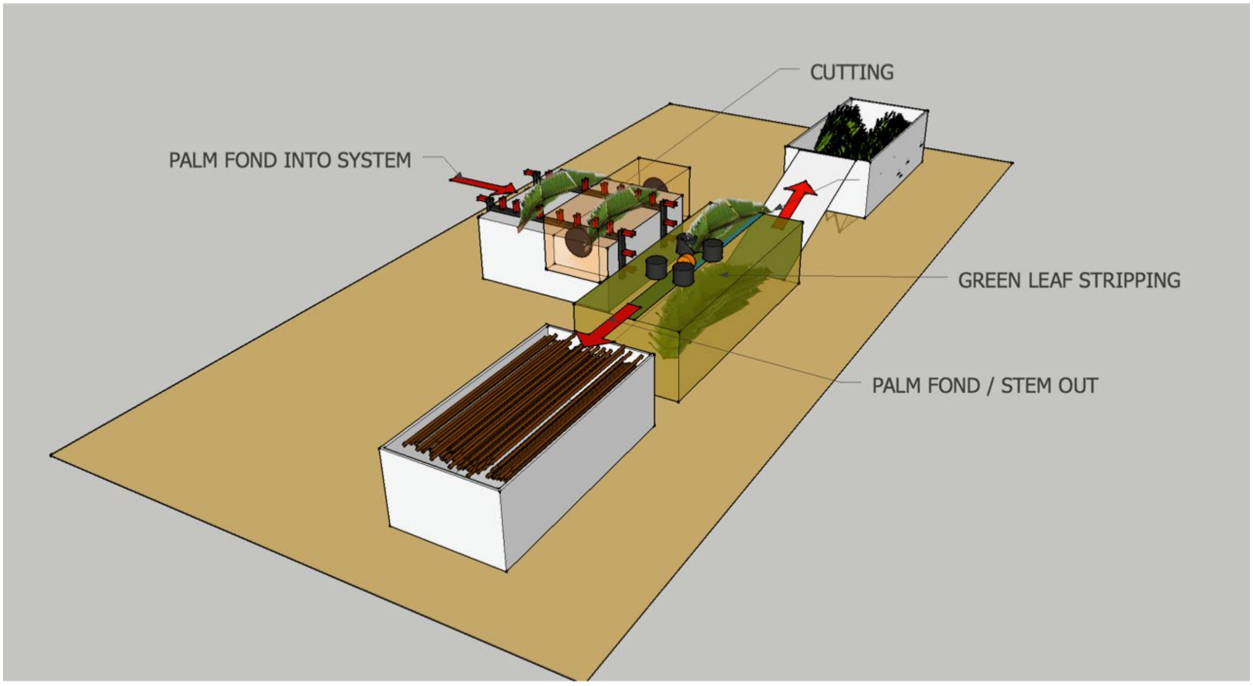

Figure 4: Automated system conceptual design

Price Estimation of the Biomass Fuel

Automation is proposed in this study to maximize the amount of waste collection during the usual 3 months of cleaning seasons in the Madina region. For an affordable price of the biomass, the supply chain must be optimized. For this purpose, 3 different collection alternatives scenarios have been developed for the implementation over a period of 5 years. The storage location for all alternatives is at Al Madina city as shown Fig. 2. The alternatives consider an establishment of a company that is specialized in fronds cleaning and biomass production. The cost includes wages, fronds collection, shipping and storing the waste. Number of staff, workers and machines defer for each alternative and accordingly the price. After the cleaning season, workers will be utilized in processing the waste to biomass. Alternative 1 is based on renting the shipping trucks, while the second and third scenarios are based on buying the trucks. For the 3rd alternative, trucks move two 20' containers at once. Starting from 20% collection of the total waste of Al Madina region in the first year, collection increases to 40% in the 2nd year and 60% in the 3rd year forward. The cost of collection is decreasing over time for all alternatives as shown in Fig. 5. However, the 3rd alternative demonstrated the best price among the other alternatives over the years.

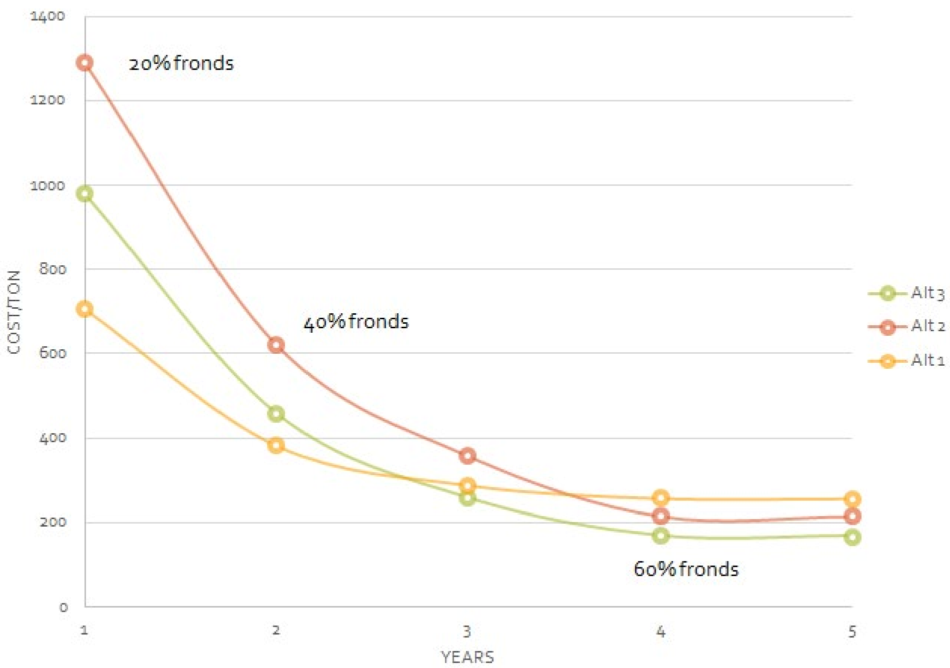

Figure 5: The cost per ton for 3 different collection alternatives scenarios over a period of 5 years

The transportation cost is estimated according to the Hino trucks, 120 L tank diesel with consumption rate of 4 km/L. Extensive trips would be required to collect the amounts of waste needed during the 3 months period of the cleaning season. Transportation costs would increase with the increase of collection amounts over the years. The capital payments of the machines, chippers, shredders, shortage and lifting devices of the containers at the storage are illustrated in table 1. It also illustrates the monthly payment of the staff, rents and bills. The annual payment is calculated based on the number of workers required for the collection process. The estimation was made based on full time manpower working all year around for the fronds collection and biomass fabrication.

Table 1: Capital and annual expenses of the collection

Cap. payment	
Machine prototype	200 k SAR
Mill wood chipper	100 k US
Mill wood shredder	100 k US
Storage building	300 K SAR
Lifting device	250 k SAR
	1.5 M SAR

	Monthly [SAR]	Annually [SAR]		
		Alt 3		
		20%	40%	60%
Management	45 k	756 k [6]	756 k [6]	756 k [6]
engineers	7 k	252 k [3]	336 k [4]	420 k [5]
Sales	6 k	72 k	72 k	72 k
Staff	6 k	288 k [4]	360 k [5]	432 k [6]
Secretary	4 k	48 k	48 k	48 k
M/C operators	3 k	540 k [15]	1 M [28]	1.3 M [35]
Truck drivers	*3 k*	*540 k [15]*	*1 M [28]*	*1.3 M [35]*
Pickup driver	1.5 k	270 k [15]	504 k [28]	630 k [35]
Workers	2 k	72 k [3]	96 k [4]	120 k [5]
Land	1 k	12 k	12 k	12 k
bill	3 k	36 k	36 k	36 k
Housing & allowances	10% salary	284 k	420 k	500 k
TOTAL		3.2 M	4.7 M	5.5 M

The lump sum of all expenses for the first 3 years are shown in table 2. The maintenance expenses of machines and trucks are estimated at 7000 SAR for every 50,000 km. The rent of pickups that carry the machines and forklifts to the farm site with associated fuel expenses are considered. The cost of collection in year 4 and 5 would settle at 169 SAR per ton because no new machines, trucks and staff are required. The cumulative number of fronds over the period of 5 years would come up to 144.2M. Assuming 1 kg weight of a frond, the average price of a collected frond would be 0.41 SAR. Adding up the inflation rate of 20% the average cost would increase to 0.5 SAR per frond.

Table 2: Total cost of the collection

[SAR]		salaries & expenses	Trucks	Diesel, trucks	Mant.*	Pickups rent	Diesel, pickup	forklift	M/C	Storage & equ.	Total	Cost/ton
Alt 3	20%	3.2 M	4.2 M	49.4 k	66.3 k	64 k	47.4 k	1.2 M	1.5 M	1.5 M	11.8 M	982
	40%	4.7 M	3.6 M	98.3 k	114.2 k	98 k	81.6 k	1 M	1.3 M	0	11 M	452
	60%	5.5 M	2 M	136 k	169.2 k	128 k	120.8 k	560 k	700 k	0	9.3 M	259

Biomass-to-Power

Generating electricity out of agricultural waste is a well known technology that is used in many countries. A biomass power plant in the UK for instance, Eccleshall generates 2.65 MW electricity for 2,600 local homes using wood chips continuous biomass feedstock brought from forestry and arboricultural 25 miles away from the plant [6]. Securing sufficient amounts of bio waste would be important for the successful implementation and operation of the power plant.

In Madina region the palm waste can be used as bio fuel for power generation. The waste at the storage location would be transformed into wood chips, briquettes and/or pellets for the use of the power plant. This feedstock would fuel the boilers that heat up the steam turbine generators. Using Siemens biomass power plant, the feedstock collected over the 5 years period would generate 12.4 MW electricity and 33.6 MW thermal heat annually. This calculation was made based on the fronds heating value of 17.25 MJ/kg [7]. The plant would consume on average 29M fronds annually. The price of such feedstock would be 14.5M SAR. With a power plant working for 300 days, 14 hours a day; i.e. 4200 hours/year, 52 TWh could be generated. The cost of biomass to generate such power would be 0.28 SAR/kWh.

Summary and Conclusion

This study investigated the feasibility of using fronds palm waste as biomass for power generation. The study was based on collecting fronds in the Madina region over the period of 5 years using automation. The price of collecting, shipping, storing and transferring the waste to biomass was investigated. Using automation would considerably maximise the amount and reduce the cost of fronds collection. Cost of using biomass as fuel for an agriculture power plant located in Madina city is 0.28 SAR/kWh. As a comparison, the cost of producing 1 kWh with diesel fuel in Saudi Arabia is about 0.21 SAR where 0.4L is required to produce 1 kWh electricity [8]. The difference in prices of both fuels are minor. However, biomass fuel could be more economically attractive with a power plant located nearby a highly populated palm area such as Al Ula city. This would reduce the transportation cost, and hence, the biomass prices.

Saudi Arabia's vision 2030 involves turning waste into electricity. Demand for this form of renewable energy projects is expected to evolve where the expected total annual production of palm fronds in the Kingdom is 1,400 thousand tons waste. This waste can produce up to 125MW of electricity and 340MW of thermal heat annually. Such an immense amount of power could be utilized with an optimised collection process serving palm farms in remote areas. Small to medium size power plants might be constructed nearby suburbs where electricity production using fossil fuel is usually costly. This would reflect on the prosperity of palm growers communities and their families where electricity would make their life easier and more settled.

References

[1] Bahruddin, Z. Helwani, & R. Martani, Study on Utilization of Palm Frond for Wood Plastic Composite, Materials Science Forum Vol. 890 (2017) pp. 40–43.

[2] Information on https://ourworldindata.org/co2/country/saudi-arabia

[3] Information on https://www.stats.gov.sa/en

[4] B. Agoudjil, A. Benchabane, A. Boudenne, L. Ibos, Magali Fois, Renewable materials to reduce building heat loss, Characterization of date palm wood, Energy and Buildings 43 (2011) 491–497.

[5] According to the Saudi General Authority for Statistics, 46% of the agricultural waste is burned in KSA.

[6] Information on https://www.eccleshallbiomass.co.uk

[7] K. Trangkaprasith and O. Chavalparit, Heating Value Enhancement of Fuel Pellets from Frond of Oil Palm, 2010 International Conference on Biology, Environment and Chemistry, vol.1 (2011), IACSIT Press, Singapore.

[8] Information on https://energyeducation.ca/encyclopedia/Diesel_generator

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Integrated Process of Ammonium Ion Adsorption by Natural Dispersed Sorbents

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Keywords: ammonium nitrogen, natural adsorbents, isotherm, adsorption kinetics, paligorskite, glauconite, zeolite.

Abstract. The process of adsorption treatment of effluents from ammonium ions is considered as an integrated two-stage process consisting of the stage of adsorption of contaminants by natural sorbents in the apparatus with a stirrer and the liquid separation stage and solid phases. Mathematical models of ammonium ions adsorption from effluents by natural dispersed sorbents are proposed, based on the assumption that the process is described by Langmuir and Friendlich isotherms. The values of ion exchange equilibrium constants for different types of natural sorbents have been established by identifying experimental data for theoretical dependences. The obtained constants can be used to calculate the average concentration of ammonium ions in the solution and in the grain of the sorbent in the process of integrated adsorption process. Based on the analysis of the research results, the optimum method of the spent sorbent separation was selected - separation of the suspension of purified ammonium-containing effluents - spent sorbent under the action of gravity. Indicators of optimization of complex process of sewage treatment from ammonium ions are offered.

Introduction

Increasing groundwater pollution by ammonium nitrogen is a dangerous trend that has developed in recent years. Ammonium-containing effluents from the chemical and petrochemical industries, the pulp and paper industry, ferrous and non-ferrous metallurgy, and insufficiently treated urban wastewater make a significant contribution to surface water pollution [1, 2]. A significant share in the pollution of surface waters with ammonium ions is also contributed by the irrational use of fertilizers that are enriched with easily soluble nitrogen compounds, pollute the hydrosphere with nitrogen compounds wastewater from livestock complexes and landfill filtrates [3, 4].

To purify wastewater from ammonia nitrogen, the following methods have become widespread: blown free ammonia, chlorination, ozonation, conversion of ammonium nitrogen NH_4^+ to molecular nitrogen N_2 biologically, removal of ammonium nitrogen by ion exchange, adsorption of ammonium ions, natural dispersions sorbents synthesized from plant raw materials [7, 8]. Analysis and comparison from the technical and economic point of view of methods extraction from aqueous solutions allows us to state that the method of ion exchange using natural dispersed sorbents is one of the most effective [9, 10]. Purification of aqueous solutions with the help of dispersed sorbents meets many requirements of environmentally friendly and energy-saving production based on the principle of non-waste. Powerful geological reserves, cheap rock extraction, easy preparation for transportation and use, the possibility of using spent sorbents in other technologies, thus eliminating the need for costly regeneration - the main advantages of using natural minerals [11, 12].

In the case of using natural sorbents to treat effluents from ammonium ions, an important task is to choose the degree of the sorbent dispersion, which is achieved through the use of appropriate grinding technologies. On the one hand, the more dispersed the sorbent, the greater the mass transfer surface and ion exchange capacity of the sorbent, on the other hand, with increasing grinding tone, it becomes more difficult to separate spent sorbent from purified aqueous medium. To assess the optimum fineness of the adsorbent grinding, the analysis of the purification process as an integrated two-stage process is promising.

We considered the integrated process of adsorption treatment of ammonium ion-contaminated effluents, which consists of two stages:

1. Adsorption of ammonium ions by natural sorbents in the device with a stirrer.
2. Separation of spent sorbents from the purified liquid medium.

Regardless of the conditions of the integrated process application in wastewater treatment technology, the criterion for its optimization is the achievement of certain treatment parameters. The optimization condition for the integrated process has the form

$$\sum_{i=1}^{n} P_i = \min \quad (1)$$

where n – the number of stages of the integrated process (for the studied integrated adsorption process n = 2); P – optimization parameter (minimum time of implementation of the integrated process, minimum consumption of sorbent, minimum cost of cleaning technology, minimum energy costs, etc.).

As a result of consideration of several possible variants of implementation strategy of the integrated process on the basis of the set parameter of purifying parameters implementing purification which provide optimum conditions for implementing process are established. The aim of these studies was to develop an algorithm for estimating the integrated process of purification of polluted aquatic environments from ammonium nitrogen by adsorption of its natural sorbents and to establish optimum parameters of such purification.

Characteristics of Materials and Research Methods

We studied natural zeolite, paligorskite and glauconite as sorbents that can be effectively used to purify effluents from ammonium ions. Samples of natural zeolite for research were taken at the Sokyrnytsia deposit (Transcarpathia). The main mineral of natural zeolite of the Sokyrnytsia deposit is clinoptilolite ($(K_2,Na_2,Ca)[Al_2Si_7O_{18}]\cdot 6H_2O$), which determines the adsorption properties of the mineral. Zeolite crystals have a system of channels and capillaries of molecular size, which determines the ability to separate mixtures of substances with molecules of different sizes and selectively purify different molecular systems. Another mineral used in the research was palygorskite from the Dashukovskoye deposit. Paligorskite ($(Mg, Al)_2[Si_4O_{10}](OH)\cdot 4H_2O$) is a clay mineral with pronounced anisotropy, as a result of which its crystals have an elongated needle shape. Under natural conditions, the primary particles of paligorskite - needles are packed in submicroscopic aggregates with a chain or oval structure. The initial structural elements of crystal lattices, which determine the adsorption properties of palygorskite, are tetra- and octahedral flat grids. Glauconite ($(K, Na)(Fe^{3+},Al, Mg)_2[(OH)_2|(Si, Al)_4O_{10}]$) of the Adamiv group of deposits in the Khmelnytsky region was also used for research. It is a mineral of the silicate class (hydromica group). Crystallizes in monoclinic syngony, layered structure.

The ammonium ions adsorption kinetics by natural sorbents was studied using model solutions prepared by dissolving NH_4Cl in distilled water, the concentration of ammonium ions in the solution was 14 mg/l. This corresponds to the real equations of ammonium ion contamination of surface waters. The research methodology consisted in reaching a certain temperature in the thermostat, which was considered to be the operating temperature of the experiment. After reaching this temperature (further the temperature was kept constant) in the flask placed in the thermostat, with the stirrer on, the test medium was loaded through the sampling device (test effluents were filled, then the test sorbent was loaded in a certain ratio to the mass of flooded effluents). The end of the sorbent loading was considered the beginning of the experiment. At intervals, samples were taken from the flask through a sampling device, filtered and analyzed. The adsorption temperature for all series of studies was maintained at 20^0C and 35^0C. The selected sample was analyzed for the content of ammonium ions by spectrophotometric methods. The SPECOL - 10 spectrophotometer with cuvettes with an optical layer thickness of 4.995 cm against the comparison solution was used for the spectrophotometric study.

Results and discussion

Langmuir's and Nikolsky's equations were used in the research to mathematically describe the equilibrium of ion exchange [13]. The following boundary conditions are accepted for these types of models:

- for the time variable: from 0 to t,
- for the variable concentration of the component in the liquid: from c_0 to c_t,
- for the variable concentration of the component in the solid phase: from 0 to q_t.

To represent the equation of the ammonium ions adsorption kinetics by natural sorbents in a form convenient for obtaining the final equations, it was assumed that the change in the mass transfer surface is proportional to the change in the complex.

Dependences describing the ammonium ions adsorption kinetics by natural sorbents were obtained by jointly solving kinetic equation (1) for the Langmuir model and (2) for the Nikolsky model, the balance equation (3) and the Langmuir (4) and Nikolsky isotherm equations (5).

$$\frac{dq_t}{dt} = k_a c_t (q_m - q_t) - k_d q_t \tag{1}$$

$$\frac{dq_t}{dt} = k_a c_t (q_m - q_t) - k_d q_t (c_o - c_t) \tag{2}$$

$$q_t = \frac{V(c_o - c_t)}{m} \tag{3}$$

$$q_e = \frac{q_m K c_e}{1 + K c_e} \tag{4}$$

$$q_e = \frac{q_m K c_e}{c_o + (K-1) c_e} \tag{5}$$

q_e, q_m, q_t - the amount of sorbed ammonium ions by natural sorbents, respectively, in equilibrium, the maximum possible for these conditions and at time t, g/100 g of sorbent; c_0, c_e, c_t - the concentration of ammonium ions in the liquid phase, respectively, the initial, in equilibrium and at time t, g/100 g of sorbent, mg/l; k_a - constant adsorption rate; k_d - constant desorption rate; V - the volume of the reaction phase, l; m - sorbent mass, g; $K = \frac{k_a}{k_d}$;

An intermediate result for the Langmuir model is the equation (6).

$$t = \frac{1}{k_a(c_{1L} - c_{2L})} \ln \frac{c_o - c_{1L}}{c_t - c_{1L}} \frac{c_t - c_{2L}}{c_o - c_{2L}} \tag{6}$$

where c_{1L}, c_{2L}, q_{1L}, q_{2L} - constants;

Equation (6) shows that there must be a linear relationship between time *t* and the $\ln \frac{c_o - c_{1L}}{c_t - c_{1L}} \frac{c_t - c_{2L}}{c_o - c_{2L}}$ complex. Using experimental data on the kinetics of sorption, this dependence can be constructed, and the tangent of the angle of inclination, which is equal to the $\frac{1}{k_a(c_{1L}-c_{2L})}$ complex, to set the k_a value.

The intermediate result of obtaining finite equations for the Nikolsky model is equation (7).

$$t = \frac{1}{k_a(1-\frac{1}{K})(c_{1N}-c_{2N})} \ln \frac{c_o-c_{1N}}{c_t-c_{1N}} \frac{c_t-c_{2N}}{c_o-c_{2N}} \tag{7}$$

where c_{1N}, c_{2N}, q_{1N}, q_{2N} - constants;

Equation (7) shows that, as for the Langmuir model, there must be a linear relationship between time t and the $\ln \frac{c_o-c_{1N}}{c_t-c_{1N}} \frac{c_t-c_{2N}}{c_o-c_{2N}}$ complex. Using experimental data on the kinetics of sorption, this dependence can be constructed and the tangent of the angle of inclination, which is equal to the $k \frac{1}{k_a(1-\frac{1}{K})(c_{1N}-c_{2N})}$ complex, to establish the k_a value.

The obtained calculation formulas for predicting the kinetics of ion exchange adsorption of ammonium ions from solution and the kinetics of sorbent saturation with ammonium ion as a result of ion exchange sorption are presented in Table 1.

For the legitimacy of the use of these equations, it is necessary at the first stage to establish the type of isotherm that most accurately describes the process of ion exchange sorption of ammonium ion on the studied type of natural sorbent. In the future, using experimental data on the sorption kinetics, it is necessary to use the obtained dependences to establish the values of the reaction rate constant, which is included in the equations shown in Table 1.

Table 1. Calculation formulas for predicting the kinetics of extraction of ammonium ions from solution and the kinetics of sorbent saturation with ammonium ions

	Equilibrium is described by the Langmuir isotherm	Equilibrium is described by the Nikolsky isotherm
The average concentration of ammonium ions in the liquid phase	$c_t = \frac{c_{2L}(c_{1L}-c_o)-c_{1L}(c_{2L}-c_o)e^{k_a(c_{1L}-\dots}}{(c_o-c_{2L})e^{k_a(c_{1L}-c_{2L})t}-(c_o-c_{1L}\dots}$	$c_t = \frac{c_{1N}(c_o-c_{2N})e^{z_{N1}t}-c_{2N}(c_o-c_{1N})}{(c_o-c_{2N})e^{z_{N1}t}-(c_o-c_{1N})}$
The average concentration of ammonium ions in the sorbent	$q_t = \frac{q_{1L}q_{2L}(e^{ak_a(q_{1L}-q_{2L})t}-1)}{q_{1L}e^{ak_a(q_{1L}-q_{2L})t}-q_{2L}}$	$q_t = \frac{q_{1N}q_{2N}(e^{z_{N2}t}-1)}{q_{2N}e^{z_{N2}t}-q_{1N}}$

where $a=\frac{m}{V}$; $z_{N1}=k_a(1-\frac{1}{K})(c_{1N}-c_{2N})$; $z_{N2}=k_a\frac{m}{V}(1-\frac{1}{K})(q_{1N}-q_{2N})$

The integrated process of adsorption of ammonium ions by natural dispersed sorbents was studied under experimental conditions using different types of natural dispersed sorbents. The kinetics of adsorption of ammonium ions by natural zeolite is presented in Fig.1.

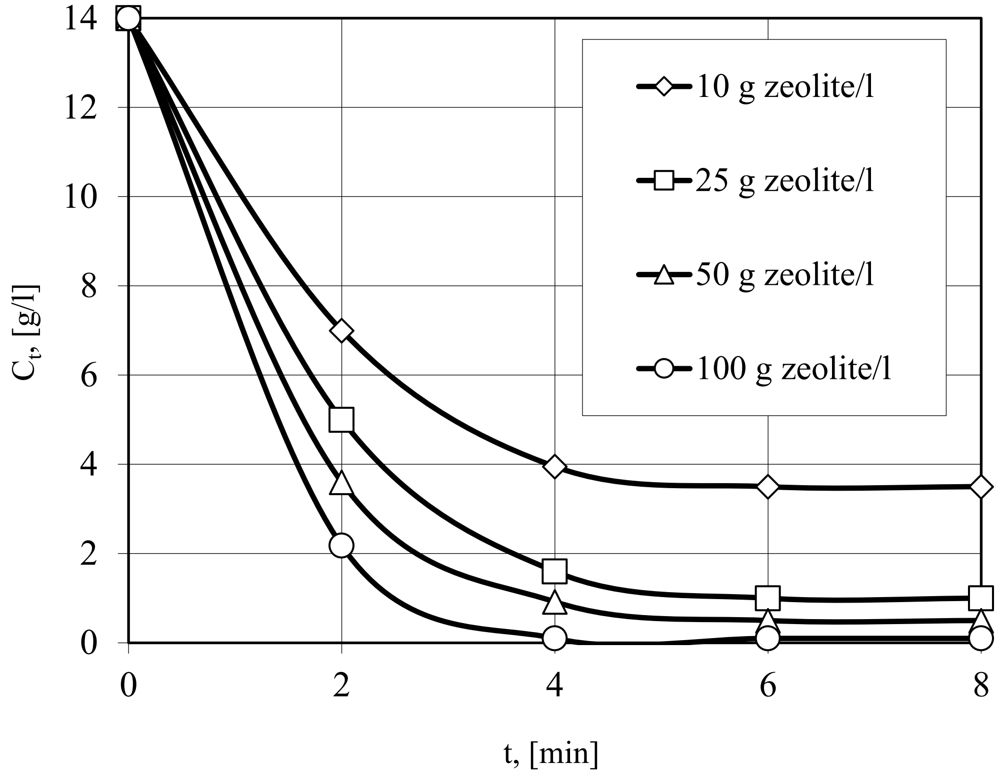

Fig. 1. Kinetics of ammonium ions adsorption by natural zeolite in an apparatus with a stirrer (temperature 20^0C).

Results similar to those shown in Figure 1 were obtained for other sorbents. Analysis of the results of experimental studies has shown that the intensity of adsorption in the direction of its reduction of the studied sorbents can be placed in a number: natural zeolite ⇒ paligorskite ⇒ glauconite.

The results of experiments showed that the maximum adsorption capacity in relation to ammonium ions is observed in the case of zeolite and palygorskite. However, the adsorption capacity of glauconite is also quite large, which allows it to be recommended for use in wastewater treatment technologies from ammonium ions. The choice of a specific adsorbent in each case should be decided by technical and economic analysis of possible options, taking into account the price of the sorbent, its adsorption capacity relative to the contaminant, the characteristics of treatment equipment.

An algorithm for the application of known calculation dependences for the analysis of experimental data on the separation of the spent dispersed sorbent from the purified liquid medium in the field of gravitational forces has been developed for the research conditions.

Adsorption isotherms were constructed for all studied systems, the form of which is presented in Fig. 2.

Based on the analysis of experimental data, it was found that in the case of zeolite and glauconite adsorbents, the experimental isotherms can be approximated by a rectilinear section of the Langmuir isotherm (Henry's Isotherm). Using Excel, trend line equations were established that looked like this:

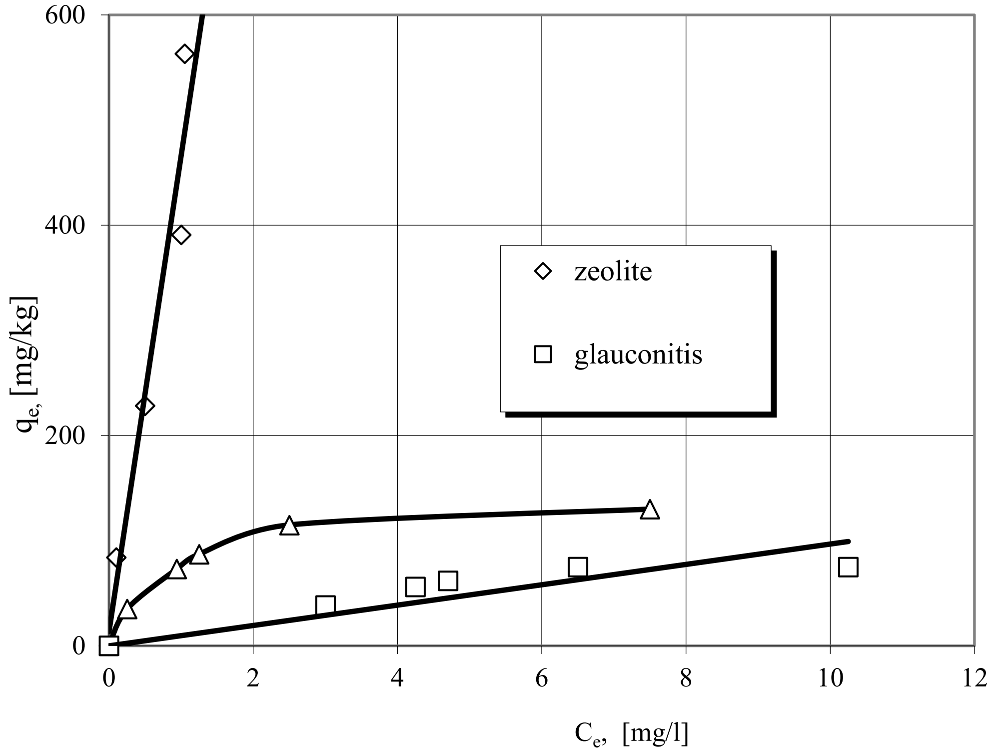

Fig. 2. Isotherms of ammonium ions adsorption in solution for different types of sorbents at temperature 20^0C.

$$q_e = K_{г} C_e \qquad (8)$$

The values of the constants for the studied cases are given in Table 2.

Table 2. Values of kinetic constants

№	Type of sorbent	Isotherm constants [m^3/mg]	Equilibrium constant of ion exchange, [1/sc]
1	Natural zeolite	$K_g = 1{,}227$	$3{,}609 \cdot 10^{-5}$
2	Paligorskite	$K_l = 0{,}9259$	$1{,}11 \cdot 10^{-5}$
3	Glauconite	$K_g = 0{,}0227$	$0{,}278 \cdot 10^{-5}$

For paligorskite, the process is described by a nonlinear isotherm, so to identify this process known theoretical models used an applied program to identify the experimental isotherm for compliance with the theoretical models of Langmuir, Nikolsky, Bi-Langmuir and Friendlich. Analysis of the identification results showed that the Langmuir isotherm describes the process most correctly.

The second stage of the integrated process was also studied - the kinetics of precipitation in treated effluents of spent, saturated with ammonium ions, particles of natural sorbents. It is established that at the initial moment of time intensive deposition of particles of large fractions takes place. This period corresponds to a rapid decrease in the concentration of sorbent in water. Then the purification intensity is reduced and is determined by the deposition rate of the particles of the smallest fraction. According to experimental data, the limiting stage of the purification process is the settling of the smallest fractions, so the rate assessment was performed for this period. The initial mass content of the sorbent in the effluent was taken as its value for the moment of transition of the process to the mode of constant low intensity of precipitation. Thus, for glauconite and zeolite this period occurred at about the 30th minute, and for palygorskite at the 10th minute. Since then, the deposition process has been characterized by a linear relationship. The sedimentation height of the particles h was determined by the design of the equipment, so in the calculations this value was taken equal to 1. The results of the calculations are shown in Table 3.

Table 3. The results of calculations of the fictitious rate of sorbents sedimentation in water

Sorbent	p	u_{cp}, [m/s]	u_{ϕ}, [m/s]
Glauconite	0,35	$4{,}86 \cdot 10^{-5}$	$1{,}39 \cdot 10^{-4}$
Paligorskite	0,31	$4{,}69 \cdot 10^{-5}$	$1{,}52 \cdot 10^{-4}$
Zeolite	0,43	$3{,}41 \cdot 10^{-5}$	$7{,}9 \cdot 10^{-5}$

The possibility of using ultrasonic spent sorbent for intensification of precipitation has been investigated. It is established that despite the slight intensification of deposition in the field of ultrasonic waves, it is impractical to use ultrasound for independent intensification of the deposition process due to the increase in energy costs. The obtained values can be used to calculate and select treatment equipment.

Regarding the implementation of the integrated process of ammonium ions adsorption by natural sorbents in general (taking into account the peculiarities of both stages), from the standpoint of implementation time, it is determined by the duration of the second stage - precipitation of spent sorbent. The duration of this stage is hundreds of times longer than the duration of the stage of ammonium ions adsorption by sorbents. Regarding the minimum sorbent costs, this optimization criterion can be realized by setting the maximum dispersion of the sorbent. However, in this case the duration of the second stage of the integrated process increases significantly. In addition, the cost of sorbent preparation increases due to the increase in energy costs for grinding.

Determining the optimization criteria should take into account the time constraints of the deposition process and the performance limitations of the unit based on whether the integrated process uses installed equipment that has certain characteristics in terms of volume costs, or plans to use a completely new installation.

Indicators of optimization of the integrated process under this strategy are:

1. Adoption of the maximum acceptable value of the duration of the integrated process of ammonium ions adsorption by natural sorbents.

2. Determination of the dispersion of the sorbent, the deposition time of which in the field of gravitational forces corresponds to this duration of the integrated process.

3. Establishment of the required amount of a certain dispersion sorbent, which will ensure the purification of effluents from ammonium ions to a given final concentration.

4. Carrying out of the technical and economic analysis of various scenarios for implementing the integrated process (taking into account current restrictions) with a choice of the most economically acceptable variant.

According to such indicators, using the established theoretical dependences, determined by identifying experimental data to the developed mathematical models, it is necessary to optimize the integrated process of wastewater treatment from ammonium ions with natural sorbents.

Spent sorbent in the future it is advisable to use in the composition of long-acting fertilizers as a carrier of ammonium ions (one of the important elements of plant nutrition). The introduction of natural sorbents into the soil environment improves soil structuring and improves their quality characteristics.

Conclusions

1. The process of adsorption treatment of effluents from ammonium ions is considered as an integrated two-stage process consisting of the contaminants adsorption stage by natural sorbents in the apparatus with a stirrer and the stage of separation of liquid and solid phases.

2. Mathematical models of ammonium ions adsorption from effluents by natural dispersed sorbents are proposed, based on the assumption that the process is described by Langmuir and Friendlich isotherms.

3. Based on the analysis of the results of experimental studies, it was found that in the case of use as adsorbents of zeolite and glauconite, experimental isotherms can be described by a rectilinear section of the isotherm (Henry's Isotherm), set Henry values. It is established that the adsorption of ammonium ions by paligorskite is most correctly described by the Langmuir isotherm.

4. The values of ion exchange equilibrium constants for different types of natural sorbents have been established by identifying experimental data to theoretical dependences. The obtained constants can be used to calculate the average concentration of ammonium ions in the solution and in the grain of the sorbent in the process of integrated adsorption process.

5. Based on the analysis of the results of the research, the optimum separation method of the spent sorbent is selected - separation of the suspension of purified ammonium-containing effluents - spent sorbent under the action of gravity. It was found that the use of ultrasound to further intensify the deposition of sorbent particles in water is impractical due to increasing energy costs.

6. The indicators of optimization of the complex process of wastewater treatment from ammonium ions are proposed, the use of which will allow choosing the optimum parameters of the process and the minimum consumption of sorbent for wastewater treatment given the allowable duration of the integrated process and the required degree of wastewater treatment from ammonium ions.

References

[1] V. Iurchenko, M. Radionov, P. Ivanin, O. Melnikova, Influence of Deep-Treated Wastewater Discharge on Nitrification Activity in a Natural Reservoirs. Journal of Ecological Engineering, 21(8) (2020) 146–155.

[2] M. Malovanyy, K. Petrushka, I. Petrushka, Improvement of Adsorption-Ion-Exchange Processes for Waste and Mine Water Purification. Chemistry & Chemical Technology, 13(3) (2019) 372–376.

[3] Y. Tulaydan, M. Malovanyy, V. Kochubei, H. Sakalova, Treatment of high-strength wastewater from ammonium and phosphate ions with the obtaining of struvite. Chemistry & Chemical Technology, 11(4) (2017) 463-468.

[4] V. Popovych, J. Telak, O. Telak, M. Malovanyy, R. Yakovchuk, N. Popovych, Migration of Hazardous Components of Municipal Landfill Leachates into the Environment. Journal of Ecological Engineering, 21(1) (2020) 52-62.

[5] H. Sakalova, M. Malovanyy, T. Vasylinych, R. Kryklyvyi, The Research of Ammonium Concentrations in City Stocks and Further Sedimentation of Ion-Exchange Concentrate. Journal of Ecological Engineering, 20(1) (2019) 158-164.

[6] M. Malyovanyy, G. Sakalova, N. Chornomaz, O. Nahurskyy, Water sorption purification from ammonium pollution. Chemistry & Chemical Technology, 7(3) (2013) 355-358.

[7] V. Ptashnyk, I. Bordun, M. Malovanyy, P. Chabecki, T. Pieshkov, The change of structural parameters of nanoporous activated carbons under the influence of ultrasonic radiation. Applied Nanoscience (Switzerland), 10(12) (2020) 4891–4899.

[8] Y. Danchenko, V. Andronov, A. Kariev, V. Lebedev, E. Rybka, R. Meleshchenko, D. Yavorska, Research into surface properties of disperse fillers based on plant raw materials. Eastern-European Journal of Enterprise Technologies, 5 (12-89) (2017) 20-26.

[9] V. Iurchenko, M. Radionov, O. Melnikova, O. Rachkovskiy, L. Mykhailova, Influence on Environmental Safety of the Drinking Water of Nitrification in Water Reservoir Being a Source of Water Supply and Filter Filling. Materials in Water Treatment Facilities, Materials Science Forum, (1006 MSF) (2020) 187-193.

[10] M. Malovanyy, H. Sakalova, T. Vasylinycz, O. Palamarchuk, J. Semchuk, Treatment of effluents from ions of heavy metals as display of environmentally responsible activity of modern businessman. Journal of Ecological Engineering, 20(4) (2019) 167-176.

[11] V. Kochubei, S. Yaholnyk, M. Bets, M. Malovanyy, Use of Activated Clinoptilolite for Direct Dye-Contained Wastewater Treatment. Chemistry & Chemical Technology, 14(3) (2020) 386-393.

[12] E.B. Ugnenko, V.A. Iurchenko, N.I. Sorochuk, O.G. Melnikova, Gintas Viselga, Study of Treatment Efficiency of Wastewater Collected from the Surface of Roads by Natural Zeolite, TRANSBUD-2019 IOP Conf. Series Materials Science and Engineering, 708 (2019) 012035.

[13] D.D. Do, Adsorption analysis: Equilibria and kinetics, Imperial College Press, London, 1998.

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Use of Natural Zeolite to Improve Quality and Environmental Safety of Natural Surface Waters and Waste Surface Waters

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Abstract. Natural zeolites are materials which, due to the peculiarities of their crystal structure and high adsorption and ion exchange properties, have wide prospects for use in technologies of adsorption purification of aquatic environments. The paper presents the results of laboratory research in dynamic and static conditions of sorption properties of natural zeolite, which is currently used for purification of natural water from suspended solids in industrial water treatment plants. The sorption capacity of different fractions of this zeolite to ammonium nitrogen, fluorides and petroleum products has been established.

Introduction

There is a wide range of available methods of natural and wastewater treatment and adsorption method is particularly effective and promising [1]. This is due to the fact that it allows you to achieve a high degree of purification at relatively low cost. The natural sorbents (zeolites, bentonites, paligorskites, glauconites) are becoming more and more widely used in water purification technologies due to their high adsorption capacity among the known sorbents. In particular, information is known on the use of bentonites to treat wastewater from chromium ions [2], ammonium [3], the use of paligorskites to purify effluents from heavy metal ions [4], the use of natural zeolites to treat wastewater from ammonium ions [5] and heavy metals [6]. Among the large number of natural sorbents, natural zeolites attract considerable attention due to the peculiarities of their crystal structure and high adsorption and ion exchange properties [7]. In Ukraine, the use of natural zeolites in adsorption technologies is highly promising because:

natural zeolites are widespread in Ukraine;

natural zeolites are an affordable, inexpensive material;

adsorption technologies are using natural dispersed sorbents provide a high degree of purification;

the natural zeolite that has been used in purification of wastewater treatment doesn't need regeneration. It will be used in technologies of reception of useful products.

Adsorption methods are promising for treatment in the process of preparation of drinking and industrial water (especially when used as a source of surface water intake) and for surface wastewater treatment before discharge into natural reservoirs [8].

The content of suspended solids and petroleum products (PP) are one of the most important indicators have influenced to the formation of surface wastewater, the nature and degree of their contamination with mineral and organic components of different origins. This type of pollutions are most important, when a technological scheme for surface runoff treatment from highways has been chosen [9].

The use of zeolites for surface wastewater treatment is regulated by the technical conditions of TU U 14.5-00292540.001-2001.When developing a scheme for drainage and treatment of surface runoff from industrial sites, the sources, nature and degree of pollution of the territory and atmosphere, size, configuration and relief of the catchment area, the availability of free space for treatment facilities, etc. are taken into account. The choice of the scheme of removal and treatment of surface runoff is based on the assessment of technical feasibility and economic feasibility of measures [10-12].

Today in Ukraine surface runoff which diverted from urban areas doesn't undergo any purification. In the best case, surface runoff is only mechanical purification from suspended solids, which doesn't remove soluble inorganic nitrogen compounds. However, the methods of sorption purification in filtration plants using specific filtrates have serious prospects [12, 13].

Among the main requirements for the safety of drinking water is the concentration of inorganic nitrogen-containing compounds (Table 1) [14, 15]. The solution to the problem of removing nitrogen compounds from natural waters using physico-chemical methods began in the 60-70's of the twentieth century. Currently, filtrants with ion exchange properties have been successfully used to remove nitrogenous compounds from wastewater [16]. However, the cost of these reagents significantly limits the application of the method. Therefore, the search for cheap materials for ion exchange wastewater treatment from ammonia nitrogen is an urgent environmental task. It is known that natural zeolite has ion exchange properties in relation to ammonium ion.

Table 1. Regulatory requirements for the concentration of nitrogen-containing compounds in drinking water

Parameter	USA	EU	WHO	Switzerland	Ukraine
Ammonium nitrogen	0.2	0.5	1.5	0.05	0.5
Nitrates	44	50	50	25	50
Nitrites	3.5	0.5	3	0.01	0.1

The concentration of inorganic nitrogen-containing compounds in surface natural water bodies (including those used for drinking water supply) is generally insignificant, in non-flowing water bodies (lakes): $N\text{-}NO_2$ – 0.01; $N\text{-}NH_4$ – 0.1; $N\text{-}NO_3$ – 0.03 mg / dm^3; in flowing reservoirs (rivers): $N\text{-}NO_2$ – 0.01; $N\text{-}NH_4$ – 0.5; $N\text{-}NO_3$ – 0.8 mg / dm^3 [17]. However, there are water bodies in which the concentrations of nitrogen compounds significantly exceed the standards [18].

Fluoride is one of the chemical elements, the microquantity of which is necessary for the proper functioning of the human body [19]. It enters the human body from many sources, but the main source of fluorine compounds is water. Its content in drinking water is strictly regulated both at the minimum and at the maximum allowable concentration: in the EU – 0.5-1.5 mg/dm^3, in Ukraine (DSanPiN 2.2.4-171-10-10 "Hygienic requirements for water drinking, intended for human consumption") [20] – 0.7-1.5 mg/dm^3.The concentration of fluorine in drinking water recommended by the World Health Organization is 0.7-1.5 mg/dm^3. However, currently in Ukraine for water consumption is widely used water with substandard fluoride content, which causes various endemic diseases. Excess fluoride in the body over a period of time can lead to the development of nervous diseases, destruction of bone tissue, accelerated aging and fluorosis, and in severe cases accompanied by bone damage to the skeleton.

To prevent mass disease of the population with fluorosis, it is advisable to carry out water defluoridation. To provide the population with physiologically complete drinking water in terms of fluoride content, a number of technical measures have been developed that serve as a man-made factor in its environmental safety.

Study Aim

The aim of the work is to establish the efficiency of natural and wastewater treatment of ammonium nitrogen, fluorides and petroleum products using natural zeolite.

Objects and Research Methods

Zeolite tuff deposits in the Zakarpattia region, which is currently successfully used at the water treatment complex in Kharkiv, were used as adsorbent in the experiments. Zeolite rocks of the Zakarpattia region deposit are represented by clinoptilolite with inclusions of montmorillonite-hydromica mite tufoargillite, quartz and feldspar. The average density of the rock is 1740-1920 kg/m^3, porosity – 20.2 - 28.1%, water absorption – 12 - 14%, compressive strength - 40 – 80 MPa [21].

Zeolite fractions were obtained by sieving. For purification we used model water environments, which were prepared on tap water. The concentration of the studied pollutants in model natural waters was created by adding the appropriate salts (ammonium nitrogen or fluorides). Model surface wastewater was prepared by emulsifying diesel fuel in distilled water with stirring with a mechanical stirrer (3 thousand revolutions per minute) for 6-7 minutes. In the model wastewater, the concentration of PP (200 mg/dm^3) was created, which is typical for rain washes from highways formed in the first 10-20 minutes of rain.

The experiments were performed under dynamic and statistical conditions. When conducting experiments under dynamic conditions (removal of $N\text{-}NH_4$ from model surface waters) used 3 fractions of zeolite with a particle size 0.315 - 2.5 mm. The height of the column backfill was 5 cm, volume 20.93 cm^3. Model laboratory surface waters with ammonium nitrogen concentration of 2-10 mg/dm^3 were treated on the laboratory filter, and 100 mg/dm^3 were determined when determining the sorption capacity. The filtration rate was 0.006-0.020 dm^3/min The ion exchange capacity of the zeolite (q, mg/g) in these experiments was set by passing through the filter certain volumes of model wastewater (from 0.5 to 7.0 dm^3) and calculating the mass of ammonium nitrogen removed from them according by the equation 1:

$$q_d = \frac{(C_1 - C_2) \cdot V}{M} \quad (1)$$

where q_d is the ion exchange capacity of the zeolite, mg/g;
V – the volume of the missed model runoff, dm^3;
M – the mass of zeolite in the filter, g;
C_1 – concentration of $N\text{-}NH_4$ in the source wastewater;
C_2 – concentration of $N\text{-}NH_4$ in purified water.

4 fractions of zeolite (≤1.1-3.3-5.0 ≥5 mm) were used in experiments on the treatment of surface wastewater generated on highways.

When conducting experiments under static conditions, 100-200 cm^3 of test water was added to conical flasks with a volume of 250 cm^3, then 2-10 g of zeolite was added to each flask (each variant in 2 replicates). The mixtures were shaken for a set time on a shutter machine. Every 20 minutes samples were taken from the flasks, filtered if necessary, and residual contaminants were determined in the filtrate. One fraction of zeolite 1-3 mm was used in experiments on purification of natural waters from fluorides. The sorption capacity of the zeolite was set in the dynamics of purification to achieve a stable residual concentration.

The statistical adsorption capacity of zeolite (A, mg/g) was determined by the equation 2:

$$A = (C_0 - C_p)/V\ m, \quad (2)$$

where C_0 and C_p – initial and equilibrium concentration of pollution, respectively, mg/dm^3;
V – the volume of the solution, dm^3;
m – the mass of the sorbent, g

The concentration of pollutants in model natural and wastewater was determined according to the methods recommended by regulations [22]: PP – gravimetric method, ammonium nitrogen photocolorimetrically with Nessler's reagent, fluorides photocolorimetrically zirconium-alizarin method.

Results and Discussion

The experimental data obtained by filtering model wastewater through a layer of natural zeolite are given in Table 2. As can be seen, experimental studies indicate the possibility of using natural zeolite to treat surface wastewater from ammonia nitrogen. The cleaning effect even when using the largest fraction of zeolite reached 100%. The most efficient model wastewater was treated from ammonium nitrogen in a filter with a filtrate that had a zeolite fraction size of 0.315-0.63 mm, which is consistent with the data of scientific and technical literature. The minimum values of contact of the treated water with the filtrate, which achieves 100% purification effect of ammonium nitrogen, were: for the fraction of zeolite 0.315-0.63 mm - 15 min, for the fraction 0.63-1.25 mm - 20 min, for the fraction 1.25-2.5 mm – 30 minutes.

Table 2. The efficiency of treatment of model surface wastewater from ammonia nitrogen when filtering through natural zeolite

Filtering time, min.	Purification efficiency (%) with the size of the zeolite fraction, [mm]		
	0.315-0.63	0.63-1.25	1.25-2.5
5	70.2	71.8	66.8
10	97.2	94.2	74.8
15	100	98.0	77.8
20	100	100	99.4
30	100	100	100

To establish the parameters of structures and technological parameters of surface wastewater treatment on ion-exchange filters, it is necessary to install the ion-exchange (sorption) capacity of the filter used - q. mg/g. To do this, a series of experiments were performed on laboratory filtration systems. The results of the experiment to determine the sorption capacity of different fractions of the filtrate are presented in Fig. 1.

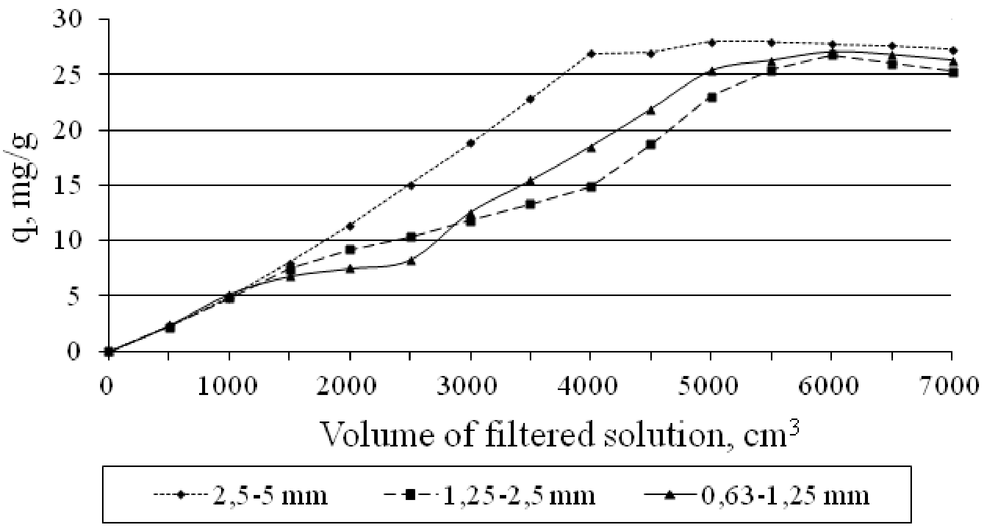

Fig. 1. Determination of sorption capacity of different fractions of natural zeolite relative to ammonium nitrogen

As can be seen, the largest sorption capacity is about 26 mg/g, has a zeolite fraction of 0.63-1.25. It was not possible to determine the sorption capacity for the zeolite fraction <0.63 mm in this experiment, because during long-term filtration of large volumes of model wastewater, the filtrate was removed from the filter.

The studied zeolite is already used at drinking water treatment facilities in Kharkiv. It is used as a backfill for quick filters to remove suspended solids. The additional effect of ammonia nitrogen removal increases the level of environmental safety of drinking water for the population. In addition, this zeolite can be used to treat surface wastewater from ammonia nitrogen before discharge into natural reservoirs. The implementation of the technology of surface runoff treatment by means of filtration through natural zeolite does not require large capital costs: you can use the existing stormwater tanks for settling.

Excess fluoride in the body over a period of time can lead to the development of nervous diseases, destruction of bone tissue, accelerated aging of the body and fluorosis - damage to tooth enamel. In Ukraine (DSanPiN 2.2.4-171-10-10 "Hygienic requirements for drinking water intended for human consumption") environmentally safe concentration of fluorides in drinking water is – 0.7-1.5 mg/dm^3 [20]. In some sources of drinking water supply the concentration of fluorides exceeds the permissible level. The results of treatment of fluorine-containing water with zeolite (fraction 1-2 mm) are presented in Table 3.

Table 3. The effectiveness of water purification from fluorides in contact with natural zeolite

Duration of contact, min	Fluoride concentration, [mg/dm^3]		
0	5.2	10,1	20.0
20	0.9	6.3	15.1
40	0.2	5.2	15.1
60	0.1	5.0	15.0

Based on the obtained results, the average sorption capacity of the studied zeolite to fluorides is 0.51 mg/g. But the main conclusion from the obtained results: the zeolite is used as a backfill in water treatment filters (Donetsk complex, Kharkiv) reduces the concentration of fluorides in drinking water to a much lower than standard level. Such technical solution is a man-made cause of increasing the environmental hazard of drinking water in terms of fluoride concentration for the population. Therefore, to prevent environmentally hazardous levels of fluoride in the water consumed by up to 75% of the city's residents, it is advisable to use a mixture of quartz sand and anthracite to fill the filters in water treatment facilities. This will increase the concentration of fluorides in tap water almost twice.

In the experiments on the purification of model washes from highways, the dependence of the rate of PP removal in the first 10 minutes of contact of wastewater with zeolites on the size of the zeolite fraction was established (Table 4). As can be seen, the highest rate of surface wastewater treatment from PP (312 mg/g • h) was observed for the smallest fraction of zeolite (≤ 1 mm). In the processing dynamics, the rate of PP removal by zeolites of all fractions steadily decreased (as noted by other authors), which is characteristic of the sorption purification mechanism.

Table 4. The rate of treatment of surface wastewater from PP in the dynamics of treatment

Zeolite fraction	PP removal rate (mg/g·h) at a treatment time of 10 [min]	Sorption capacity in relation to PP, [mg/g]
≤ 1 mm	31.,2	0.5
1-3 mm	19.5	0.7
3-5 mm	11.7	1.25
≥5 mm	9.3	2.0

The sorbitol capacity of the zeolite in relation to the PP, established in the experiments, corresponds to the results of studies of various zeolite tuffs performed by other authors.

The introduction methods of cleaning washes from highways using natural zeolites solves the important problem of improving the technical level of highways, traffic safety and environmental safety of these technical facilities.

Conclusions

The obtained data of experimental researches testify that natural zeolite has sorption ability to ammonium nitrogen (ion exchange), fluorides and petroleum products. This property is promising for use in water treatment (natural water treatment for drinking water) and surface wastewater treatment (especially road washes). However, when using natural zeolite for water treatment, it is necessary to take into account its sorption properties to fluorides and the concentration of fluorides in water intended for drinking water use to prevent the creation of fluoride deficiency.

References

[1] E. Bazrafshan, P. Amirian, A.H. Mahvi, A. Ansari-Moghaddam, Application of adsorption process for phenolic compounds removal from aqueous environments: a systematic review. Global Nest Journal, 18(1) (2018) 146–163.

[2] M. Malovanyy, O. Palamarchuk, I. Trach, H. Petruk, H. Sakalova, Kh. Soloviy, T. Vasylinych, I. Tymchuk, N. Vronska, Adsorption Extraction of Chromium Ions (III) with the Help of Bentonite Clays. Journal of Ecological Engineering, 21(7) (2020) 178-185.

[3] H. Sakalova, M. Malovanyy, T. Vasylinych, R. Kryklyvyi, The Research of Ammonium Concentrations in City Stocks and Further Sedimentation of Ion-Exchange Concentrate. Journal of Ecological Engineering, 20(1) (2019) 158-164.

[4] L. Melnyk, O. Bessarab, S. Matko, M. Malovanyy, Adsorption of heavy metals ions from liquid media by palygorskite. Chemistry & Chemical Technology, 9(4) (2015) 467-470.

[5] M. Malyovanyy, G. Sakalova, N. Chornomaz, O. Nahurskyy, Water sorption purification from ammonium pollution. Chemistry and chemical technology, 7(3) (2013) 355-358.

[6] M. Malovanyy, K. Petrushka, I. Petrushka, Improvement of Adsorption-Ion-Exchange Processes for Waste and Mine Water Purification. Chemistry & Chemical Technology, 13(3) (2019) 372–376.

[7] I. B. Zasidko, M. S. Polutrenko, O. M. Mandryk, Use of zeolite for cleaning of natural water and effluents of communal enterprises. Scientific Bulletin of UNFU, 27(5) (2017) 63–66.

[8] Larysa Mykhailova, Valentina Iurchenko, Thomas Fischer, Deposition of petroleum hydrocarbons with sediment trapped in snow in roadside areasю. Journal of Environmental Engineering and Landscape Management, (2014) 1–9.

[9] E. Ugnenko, V. Yurchenko, N. Sorochuk, O. Melnikova, G. Viselga, Study of Treatment Efficiency of Wastewater Collected from the Surface of Roads by Natural Zeolite. TRANSBUD-2019 IOP Publishing IOP Conf. Series: Materials Science and Engineering, **708** (2019) 012035.

[10] V. Hvat, M. Manuylov, V. Medvedev, Ispolzovanie poverhnostnogo stoka v sistemah promvodosnabzheniya pri ustroystve malostochnyih proizvodstv, Materialyi 3-y Respublikanskoy nauchno-prakticheskoy konferentsii «Zamknutyie tehnologicheskie sistemyi vodoispolzovaniya i utilizatsiya osadkov vod v promyishlennosti», (1990) 103-105 [in Russian].

[11] Rekomendatsii po raschetu sistem sbora, otvedeniya i ochistki poverhnostnogo stoka s selitebnyih territoriy, ploschadok predpriyatiy i opredeleniyu usloviy vyipuska ego v vodnyie ob'ektyi. [Elektronnyiy resurs] /Rezhim dostupa: http://www.gostrf.com/Basesdoc/50/50785/index.htm [in Russian].

[12] Rekomendatsiy zabezpechennya efektivnogo vidvedennya miskih zlivovih stokiv ta viznachennya parametriv ochisnih sporud. Posibnik do DBN. Zatverdzheniy: Nakazom Ministerstva z pitan zhitlovo-komunalnogo gospodarstva Ukrayini vid 14.10.08, № 302 [in Ukraine].

[13] Ulashtuvannya poverhnevogo vodovidvedennya na teritoriyah mist i selisch SOU ZhKG 41.00-35077234. 0018:2009. Priynyato ta nadano chinnosti: nakaz Ministerstva z pitan zhitlovo-komunalnogo gospodarstva Ukrayini [in Ukraine].

[14] N. Espejo-Herrera, K. Cantor, N. Malats, D. Silverman, A. Tardón, R. García-Closas, C. Serra, M. Kogevinas, C. Villanueva, Nitrate in drinking water and bladder cancer risk in Spain. Environmental Research, 137 (2015) 299–307.

[15] Nitrate and Nitrite in Drinking: A Toxicological Review, Water California Environmental Protection Agency. Oakland, CA, USA, 2011, pp. 139–145.

[16] M. Sprynskyy, M. Lebedynets, A. Terzyk and al., Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. J. of Colloid and Interface Science, 284 (2005) 408-415.

[17] A. Ryizhakov, Kineticheskie harakteristiki transformatsii azotsoderzhaschih soedineniy v prirodnoy vode. Ekologicheskaya himiya, 21(2) (2012) 117–124. [in Russian].

[18] V. Iurchenko, M. Radionov, P. Ivanin, O. Melnikova, Influence of Deep-Treated Wastewater Discharge on Nitrification Activity in a Natural Reservoirs. Ecological engineering: Scientific journal, 21(8) (2020) 146–155.

[19] Fluoride. Dietary Reference Intakes: Calcium, Phosphorus, Magnesium, Vitamin D, and Fluoride. Institute of Medicine. Washington D.C.: National Academy Press. 1997, pp. 288-313.

[20] DSanPIN 2.2.4-171-10 "Gigienichni vimogi do vodi pitnoyi, priznachenoyi dlya spozhivannya lyudinoyu". Zareestrovano v Ministerstvi yustitsiyi Ukrayini i lipnya 2010 r. po N 452/17747. -39 s. [in Ukraine].

[21] A. Givlyud, V. Sabadash, Ya. Gumnitskiy, Obgruntuvannya mozhlivosti vikoristannya prirodnogo tseolitu dlya ochischennya stichnih vod molokozavodiv. Visnik Lvivskogo derzhavnogo universitetu bezpeki zhittediyalnosti, 12 (2015) 185-190. [in Ukraine].

[22] List of methods for performing measurements (determinations) of the composition and properties of samples of environmental objects, emissions, wastes and discharges provisionally allowed for use by the State Inspectorate of Ukraine, approved by the Head of the State Environmental Inspectorate of Ukraine - Chief State Inspector of Ukraine for Environmental Protection on 01.03.2013 [in Ukraine].

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Studies of Adsorption Capacity of Montmorillonite-Enriched Clay from the Khmelnytskyi Region

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Keywords: montmorillonite, thermal analysis, X-ray phase analysis, adsorption, cationic dyes

Abstract. Clay from the Khmelnytskyi region was enriched in montmorillonite by separation of a fraction with a particle size $\leq 0.5 \cdot 10^{-6}$ m. The X-ray diffraction and thermal analyses suggest that the enriched clay composition is close to mono-mineral, that is, represented by ferric-type montmorillonite in the form of Ca and Mg. The mineral interlayer spacings are partially filled with natural organic matter. An exchange capacity of montmorillonite is 0.78 mmol/g as shown by the photocolorimetry studies of the adsorption of the cationic methylene blue (MB) dye. It is recommended that studied clay be used as an effective natural adsorbent for wastewater treatment and for the arrangement of geochemical barriers to prevent harmful substances from entering the environment.

Introduction

Bentonites are defined as clay material, composed predominantly of minerals of the montmorillonite group. Montmorillonites are labile minerals with apparent cation exchangeable properties. Due to the active centers of basal surfaces, the montmorillonite structure is prone to sorb inorganic compounds and molecules of organic substances [1, 2]. Neutral organic ligands can form complexes with interlayer cations. The cations of the montmorillonite exchange complex can come into the ion exchange with various organic cations [3, 4]. These processes cause an expansion of the mineral structure-swelling.

High ion exchange, adsorption, and swelling properties facilitate the wide use of bentonites in a variety of industry and agriculture branches.

Bentonites are used for the disposal of industrial waste, in particular spent nuclear fuel [5], the prevention of the migration of radionuclides and other toxic substances [6], and wastewater treatment for environmental purposes [7]. Modifying bentonite clays with organic substances results in effective organo-mineral adsorbents, being widely used to remove heavy metal ions from wastewater [8].

Clays are multicomponent systems represented by diverse associations, from clay and non-clay minerals, amorphous organic compounds to inorganic substances. The determination of clay properties hinges on the clay mineralogical composition and geological conditions under which they were formed. As a new deposit is explored, it is important to remove a dominant clay mineral whose structure, adsorption capacity, and nature of the cation exchange complex are to be studied.

Ukraine has industrial deposits of bentonite clays in the Dniprovsko-Donetsk and Transcarpathian depressions, the Carpathian foredeep, and the Volyn-Podilsk upland [9]. Special attention is paid to clay deposits from industrial agglomerations. They have a tough environmental situation and a well-developed transport network. These deposits include clays from the left side of the upper Pivdennyi Bug river, not far from the city of Khmelnytskyi.

Besides deposits, there is also a range of food processing plants and a paperboard mill, releasing a huge amount of industrial wastewater. The Khmelnytskyi region has a running nuclear power plant that acts as a source of radioactive waste.

Over 750 landfills occupy the territory of the Khmelnytskyi region, of which six landfills are overloaded and need to be expanded or closed. Due to imperfect project design, the existing landfills pose a potential threat to the environment. They operate without impervious screens and systems for removing and cleaning filtrate [10, 11].

The presence of deposit of cheap montmorillonite-enriched clay close to Khmelnytskyi will address many important environmental issues.

Synthesis methodology and sample examination

The object of the paper is to study clays from the forest-steppe zone of the Volyn-Podilsk upland. These clay deposits do not come to the surface but are examined only through exploratory wells. Geological engineering surveys are carried out in the Northwestern part of Khmelnytskyi, towards the village of Oleshyn.

Studied clay was enriched in montmorillonite by sedimentation of the coarsely dispersed phase. The clay was preliminary purified in distilled water at a 1:10 liquid-to-solid ratio. The suspension was allowed to stand for 20 minutes. Then the upper layer was collected as it contained clay minerals.

Clay was enriched in montmorillonite by way of centrifugation of clay suspensions for 12 minutes (1000 rpm). After centrifugation, the suspension obtained was precipitated and the precipitate separated. In this case, the clay fraction of $\leq 0.5 \cdot 10^{-6}$ m was obtained.

For X-ray diffraction analysis of investigation, the ADP-2.0 diffractometer (Fe anticathode and Mn filters, 30 kV and 12 mA) was used. The analysis was made on the oriented specimens of a fine pelite fraction: air-dried saturated ethane-1,2-diol that was burned at 550 °C for 1 hour; organic clays that were formed at various initial concentrations of MB dye solutions.

For the complex thermal analysis, the Q-1500 derivatograph of the Paulik-Paulik-Erdey system connected to a personal computer was used. The analysis was made on the samples of natural pelite and organic montmorillonite. The latter was obtained as a result of adsorption of MB clay with a particle of $\leq 0.5 \cdot 10^{-6}$ m. The studies were carried out at the range from 20 to 1000°C in air. The heating rate of the samples was 5°C per minute. Before the thermal analysis, the samples were dried at 50°C. For various fractions of natural pelite, the mass of samples was 500 mg while for the organo-mineral complex 200 mg. Aluminum oxide was used as a reference substance.

The adsorption of MB dye took place under the following conditions: 50 cm^3 of MB solution of known concentration was added to the air-dried samples of enriched clay of 0.1 g. Then the system was stirred. After a two-day cycle (a time enough to reach equilibrium), the equilibrium solution was removed from the dispersed phase by centrifugation. The adsorption value was determined as a difference between the concentrations of initial and equilibrium dye solutions. The equilibrium concentration was found by using the T-105 photocolorimeter with a light filter of 582 nm wavelength.

Results and Discussions

The X-ray diffraction analysis suggests that the clay fraction with a particle of $\leq 0.5 \cdot 10^{-6}$ m is close to mono-mineral. It is represented by montmorillonite with admixtures of illite and kaolinite. Of non-clay minerals, traces of quartz and calcite were found. (Fig.1).

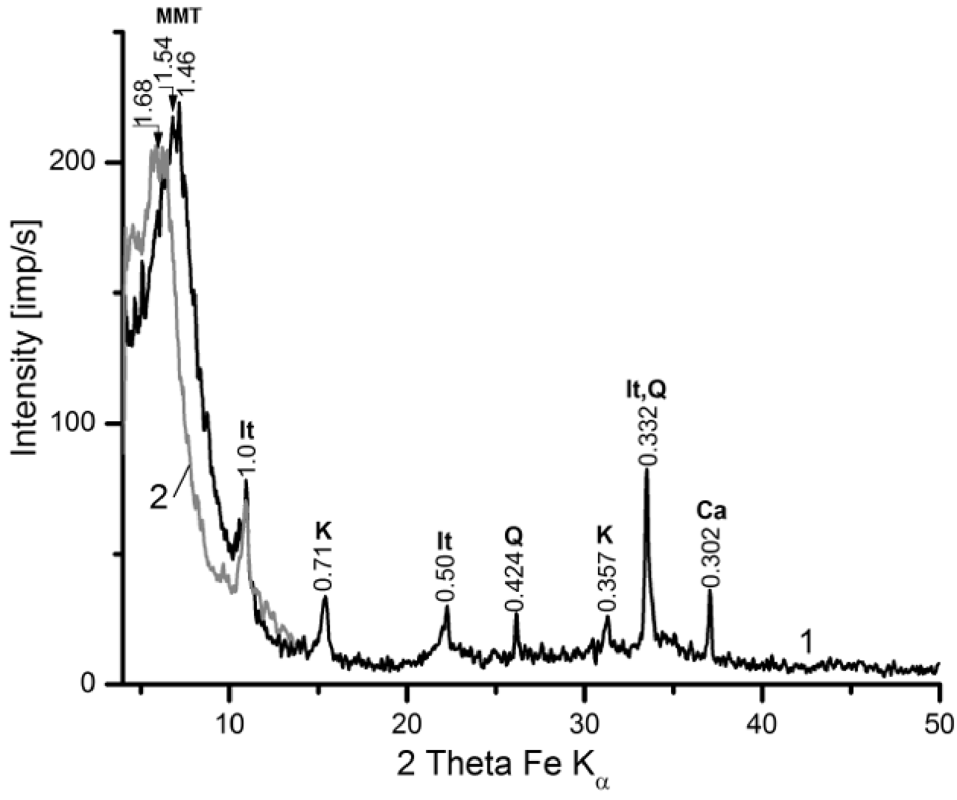

Fig. 1. Diffraction curves of oriented specimens of enriched clay: 1 – air-dried, 2 – saturated ethane-1,2-diol. Minerals: MMT – montmorillonite, It – illite, K – kaolinite, Ca – calcite, Q – quartz

A top of the 001 reflex of montmorillonite records the lines, such as 1.54 and 1.46 nm, which characterize Ca and Mg – a form of montmorillonite. An extremum that corresponds to the interlayer distance of 1.54 nm is attributed to the presence of Ca^{2+} exchangeable cations in the mineral structure. The line with 1.46 nm d/n reflects the presence of Mg^{2+} in exchangeable positions [12]. When saturated with ethane-1,2-diol ($C_2H_4(OH)_2$), the interlayer distance rises to 1.68 nm. This corresponds to the injection of two layers of adsorbate molecules into interlayer spacings. An increase in d (001) once again confirms that the mineral exchange complex has ions with the coordination number 6: Ca^{2+} and Mg^{2+}. A set of lines – 1.78, 1.84, 2.21, and 2.41 nm – indicates the presence of natural organic matter (Fig. 3, curve 1) in the interlayer spacing of montmorillonite.

Based on the low-intensity reflexes, there were identified insignificant impurities of illite (1.0; 0.45 and 0.332 nm); kaolinite (0.71 and 0.357 nm); pelitomorphic quartz (0.424; 0.332); and calcite (0.302 nm).

The X-ray diffraction findings on the montmorillonite-enriched clay samples are supported by the thermal analysis. Fig. 2 shows a thermogram of the sample of the clay fraction with a particle of $\leq 0{,}5\cdot10^{-6}$ m.

The mass loss of the montmorillonite-enriched clay sample (6.20%) within 20-220°C accrues to the release of interlayer water by clay minerals. This process is followed by a deep endothermic effect in the DTA curve. The DTG curve exhibits a sharp extremum with an inherent bend at 159°C. This means that montmorillonite carries exchangeable cations that are Ca–Mg in nature. At temperatures lower than 159°C, the Ca–Mg form of montmorillonite loses the first layer of coordinated water molecules. The next layer of water molecules is lost at higher temperatures [13].

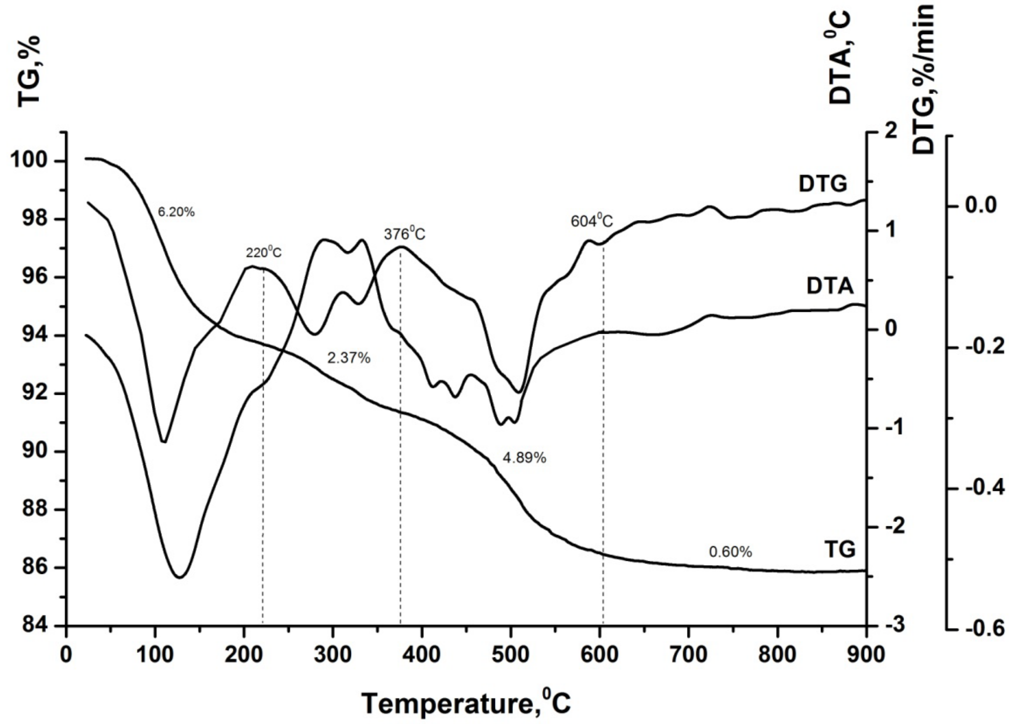

Fig. 2. Thermogram of enriched clay sample

Within the range of 220-376°C we observe the thermal-oxidative destruction of the natural organic matter that is absorbed by the surface of sample particles. This process is accompanied by an exothermic effect that appears in the DTA curve and a double extremum in the DTG curve. This double extremum indicates bound organic matter is complex in nature [14].

The mass loss (4.89%) of enriched clay samples in the temperature range of 376-604°C refers to the release of constitutional water by montmorillonite – a key clay mineral. The low thermal stability of montmorillonite accrues to the greater amount of Fe^{3+} in the octahedral positions. Isomorphic replacement of Al^{3+} and Mg^{2+} by Fe^{3+} decreases the thermal stability of montmorillonite and shifts dihydroxylation to occur in a region of low temperatures [15]. Destruction of the montmorillonite structure is followed by the combustion of natural organic matter, being adsorbed by labile intervals of montmorillonite.

The destruction of the montmorillonite structure and combustion of organic matter residues takes place further within the range of 604-800°C. After that, the sample mass loss is gradual, amounting to 0.6%.

Thus, the X-ray diffraction and thermal analyses found that the clay fraction with a particle of ≤ $0,5\cdot10^{-6}$ m is primarily represented by the Ca–Mg form of montmorillonite as a key mineral. The interlayer spacings of montmorillonite are partly filled with natural organic matter that is sorbed under natural conditions.

To determine the ion-exchange capacity of montmorillonite as the main constituent of clay, the researchers studied the adsorption of the cationic MB dye by a photocolorimetry method. Fig. 3 shows an isotherm of the MB adsorption by the enriched clay sample.

The cation exchange capacity (CEC) of clay of 0.78 mmol/g was measured based on the maximum adsorption value. A logical explanation for the appreciably smaller CEC value is the presence of natural organic matter in the labile spacings of montmorillonite.

The cation exchange plays a prominent part in the sorption of organic cations by bentonites. However, the distribution of organic cations on the silicate surface can be attributed not only to electrostatic but also to van der Waals interactions that occur between the alkyl chain and the basal surface of montmorillonite [16]. Molecules of organic compounds can penetrate the interlayer spacing containing organic matter in the form of simple components as reported by recent works of various scientists [17]. As the adsorption of MB dye occurs within the interlayer spacing of montmorillonite, an organo-mineral complex – methylene blue-montmorillonite – is formed.

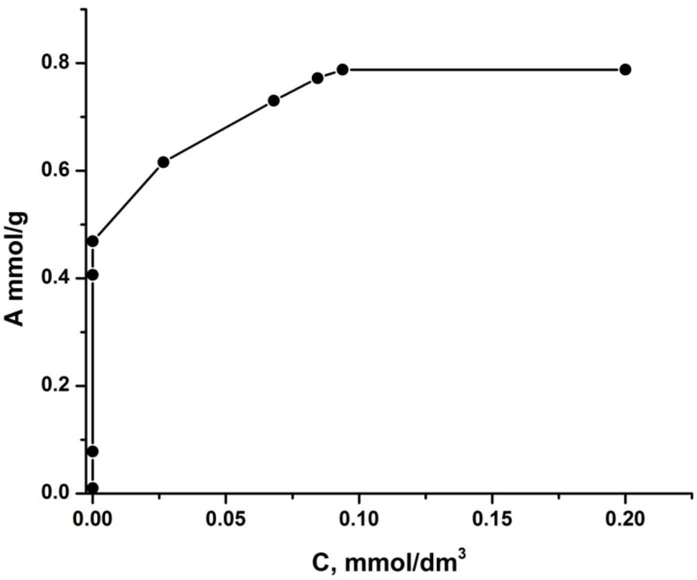

Fig. 3. Isotherm of the MB dye adsorption by the enriched clay sample

The size of organic cations and the layer charge of silicate have a significant effect on the capacity of such cations for placement within the mineral interlayer spacing. This charge results from the isomorphic replacement of Al^{3+} cations in the octahedral positions of montmorillonite. As a moderate concentration of silicate layer charge is typical of montmorillonite, the cations of the MB dye can lie flat in one layer on the silicate surface. In this case, the exchangeable positions retain partly the ions of Ca^{2+} and Mg^{2+} and water molecules coordinated by such ions [18].

In case of complete displacement of natural exchangeable inorganic cations and water molecules coordinated by such cations, methylene blue cations can be packed in two layers in the mineral's labile spacings. Under such conditions, organic cations completely compensate for the silicate layer charge. It is important that the interlayer distance of montmorillonite be 1.76 nm provided that the silicate layer thickness is 0.92 nm and transverse dimensions of methylene blue molecules are 0.42 nm [19].

Fig. 4 shows the findings of the X-ray diffraction analysis of the enriched and organic clay samples. The organic clay is formed as a result of the adsorption of the MB dye.

At low initial concentrations of 0.78 mmol/dm^3 of the MB dye in the solution, the main basal reflex expands and shifts to the area of small angles (Fig. 4, curve 2). The reflex intensity decreases appreciably due to the heterogeneity of the montmorillonite structure. This indicates that interlayer spacing within the mineral structure varies in thickness. Some spacings still retain the natural cation exchangeable complex while others are intercalated with the dye ions and have Ca^{2+} and Mg^{2+} partly retained in exchangeable positions.

For the initial MB concentration of 3.44 mmol/dm^3 (curve 3), part of montmorillonite interlayer distances expands to 1.78 nm and rises to a gentle plateau. This means that two layers of MB organic cations are formed in liable spacings of montmorillonite. For the initial MB concentration of 6.25 mmol/dm^3, the reflex intensity of 1.78 nm increases noticeably. This indicates the greater amount of interlayer spacings in which two layers of methylene blue molecules are formed after the full cation exchange (curve 4).

The slope of the main reflex of the diffractometry curves of organic clay has lines that correspond to the following interlayer distances: 1.84; 1.91; 2.05; 2.21; 2.41; and 2.51 nm. These lines are shifted to the region of small angles unlike those similar lines of 1,78; 1,84; 2,21; 2,41 nm in the spectrum of the initial clay sample (curve 1). The explanation for increased interlayer distances is the partial intercalation into the labile spacing of montmorillonite that has organic matter and MB dye molecules.

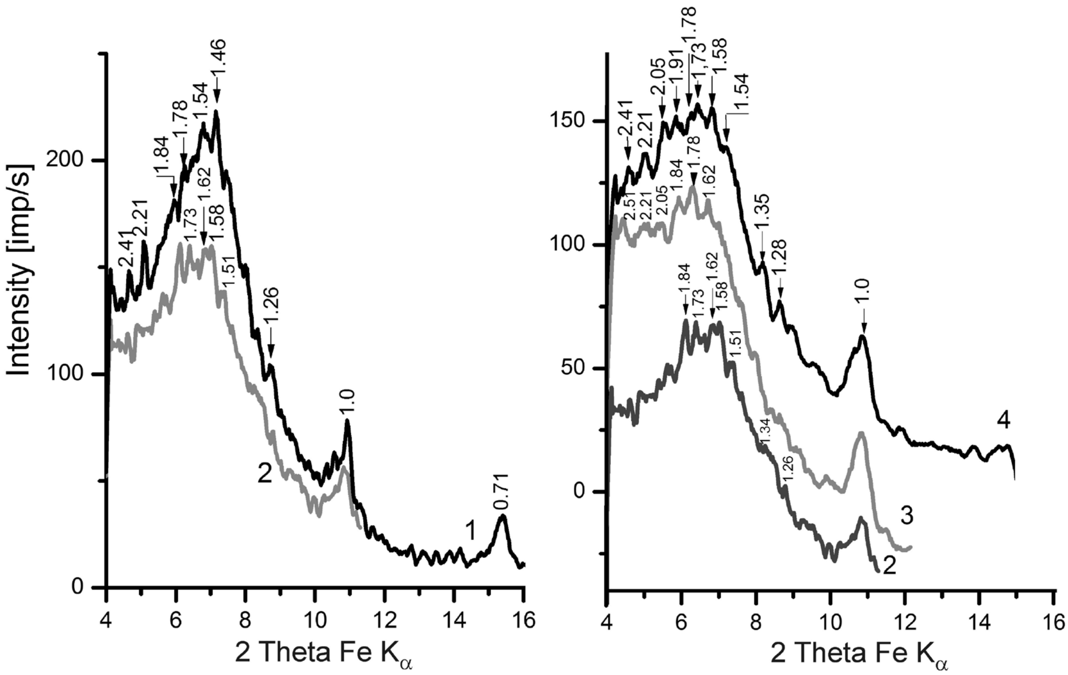

Fig. 4. Diffractometry curves for the oriented specimens: 1 – air-dried enriched clay; organic clay formed at various initial concentrations of MB with the following values: 2 – 0.78 mmol/dm^3, 3 – 3.44 mmol/dm^3, 4 – 6.25 mmol/dm^3

Based on the X-ray diffractometry studies, it can be concluded that after adsorption of the MB dye by montmorillonite organic clay has a complex structure. This structure has interlayer spacings in which the partial or full exchange of inorganic cations for methylene blue ions took place. There are also those interlayer spacings that are filled with natural organic matter and partly intercalated by methylene blue. The remaining spacings had no ion exchange; instead, they have the natural exchangeable complex of Ca^{2+} i Mg^{2+} retained. An explanation for the variety of interlayer spacings is that they contain natural organic matter with a complex structure and capacity to block access to these spacings.

Conclusions

The findings imply that a finely dispersed fraction of ≤ 0,5 10^{-6} m of clay from Volyno-Podillya is close to mono-mineral – represented by montmorillonite. Ferric-type montmorillonite is a mineral whose exchangeable positions retain Ca^{2+} and Mg^{2+}. Montmorillonite has a low exchange capacity of 0.77-0.78 mmol/g that is due to the presence of adsorbed natural organic matter in the mineral's labile interlayer spacings.

The capacity of the studied clay material to absorb cationic forms of organic compounds is recommended to be used for wastewater treatment by removing environmentally harmful dyes and organic compounds.

Clay from the Khmelnytskyi region can be used for the protection of landfills from the filtrate by installing impervious screens. It is recommended that the studied clay be used as an effective natural sorbent in environment-related measures to eliminate accidents and restore territories.

References

[1] A.K. Mishra, Bentonite: characteristics, uses, and implications for the environment, Nova Publishers, New York, 2015.

[2] M. Malovanyy, K. Petrushka, I. Petrushka, Improvement of Adsorption-Ion-Exchange Processes for Waste and Mine Water Purification. Chemistry & Chemical Technology, 13(3) (2019) 372-376.

[3] G. Lagaly, M. Ogawa, I. De´ka´ny, Clay Mineral Organic Interactions, in: F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of Clay Science, Elsevier, Amsterdam, 2006, pp.309-378.

[4] R.T. Rajkiran, C.K. Kartic, N. Upendra, Synthesis and characterization of novel organo-montmorillonites. Applied Clay Sci, 38 (2008) 203-208.

[5] A. Mockovčiakova, Z. Orolínová, J. Škvarla, Enhancement of the bentonite sorption properties, Journal of Hazardous Material, 180 (2010) 274-281.

[6] T.V. Dudar, S.P. Buhera, V. M. Kadoshnikov, B.P. Zlobodenko, Barierni vlastyvosti pryrodnykh hlynystykh mineraliv. Visnyk NAU, 1 (2009) 56-60.

[7] L. Borgnino, M.J. Avena, C.P. De Pauli, Synthesis and characterization of Fe(III) montmorillonites for phosphate absorption. Colloids and Surfaces A: Physicochem Eng. Aspects, 341 (2009) 46-52.

[8] V. Mittal, V. Herle, Physical adsorption of organic molecules on the surface of layered silicate clay platelets: A thermogravimetric study. Journal of Colloid and Interface Science, 327(2) (2008) 295-301.

[9] V.A. Mykhailova, Nemetalichni korysni kopalyny Ukrainy, V.Ts. «Kyivskyi universyteta», Kyiv, 2007.

[10] P.A. Sablii, Fizyko-khimichne ta biolohichne ochyshchennia vysokokontsentrovanykh stichnykh vod, NUVHP, Rivne, 2013.

[11] Stan navkolyshnoho pryrodnoho seredovyshcha Khmelnytskoi oblasti, Khmelnytska oblasna derzhavnv administratsiia, Khmelnytskyi, 2021.

[12] D.M. Moore, R.C. Reynolds, X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, New York, 1997.

[13] Z. Ding, R.L. Frost, Controlled rate thermal analysis of nontronite. Thermochim Acta, 389(1-2) (2002) 185-193.

[14] Ya. Yaremchuk, V. Kochubei, Osoblyvosti termichnoi dehidratatsii hlynystykh mineraliv Badenskykh hipsiv iz karieriv Shchyrets i Pisky. Mineralohichnyi zbirnyk, 60(2) (2010) 106-115.

[15] V.V. Goryushkin, Tekhnologicheskie svojstva bentonitov paleoczena Voronezhskoj anteklizy i vozmozhnosti ikh izmeneniya. Vestnik Voronezhskogo universiteta. Geologiya, 1 (2005) 166-177.

[16] A.O. Holembiovskyi, A.M. Brezitska, L.M. Sokolova, Zmina struktury poverkhni montmorylonitu pry adsorbtsii kationnykh poverkhnevo-aktyvnykh rechovyn. Vostochno-evropejskij zhurnal peredovykh tekhnologij, 4/6(70) (2014) 53-57.

[17] K.Y. Jacobs, R.A. Schoonheydt, Time dependence of the spectra of methylene blue clay mineral suspension, Langmuir, 17 (2001) 5150-5155.

[18] M.F. Brigatti, E. Galan, B.K.G. Theng, Structures and mineralogy of clay minerals, Handbook of Clay Science, Elsevier, Amsterdam, 2006, 19-86.

[19] Yu.I. Tarasevich, F.D. Ovcharenko, Adsorbcziya na glinisty`kh mineralakh. Naukova Dumka, Kiev, 1975.

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Investigation of Clinoptylolite Ion Exchange Capacity Relative to Copper and Zinc Ions in Conditions of Ideal Intermixing Mode

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Keywords: clinoptilolite, copper ions, zinc ions, ion exchange, kinetics, process, modification.

Abstract. The sorption method of purification of flushing water from non-ferrous metal ions in galvanizing-bath rooms of mechanical facilities was investigated, which is one of the most realistic ways to solve the problem of environmental protection from such pollution. The effect of preliminary thermal and chemical modification of the crystal structure in order to improve the sorption capacity of clinoptilolite was established. The kinetics of the copper ion exchange process on clinoptilolite in static conditions was determined.

Introduction

Contaminated with non-ferrous metal ions waste water is formed in many industries, but one of the most voluminous sources of their formation is the washing of details in the process of electroplating. Qualitative and quantitative composition of waste water varies greatly. According to data [1], industrial effluent can contain from 80-100 g/dm^3 (concentrated exhausted solutions of the etching basins) to 10 g/dm^3 (flushing water of the rinsing baths) of copper ions. Concentration methods are used, when the metal can be returned to production in the form of a solution of its compounds of a certain concentration, and in other cases the reagent treatment methods followed by separation of purified water are used. However, reagent purification does not allow to reach the level of the maximum allowable concentration. Actual concentrations of metal ions after precipitation can reach tens or more mg/dm^3. Particular difficulties in the extraction of some toxic metals occur when they are in different ionic and valence forms (soluble ions of chromium, cadmium, nickel, copper or zinc depending on the method of coating parts) and in complex mixtures in the presence of components capable of competitive sorption.

The most common methods of heavy metal recovery include adsorption, ion exchange, membrane method, reverse osmosis [2, 3]. There are technological solutions for ion exchange waste water treatment immediately after rinsing baths, in the case when these waters contain no more than one or two types of non-ferrous metals [4, 5]. The existing local treatment plants include small-sized adsorbers, as well as equipment for neutralization of the formed regenerated solutions or electrolyzers for the extraction of non-ferrous metals (depending on the method of metal utilization). Strong acid cation exchange resins in hydrogen or salt forms, weak acid cation exchange resins in salt form and complexones are usually used as the sorbent.

The purpose of the work was to research the sorption of copper and zinc ions by natural or modified clinoptilolite and to establish the optimal modes of this process. The effect of preliminary thermal and chemical modification of the crystal structure to improve the sorption capacity of clinoptilolite has been researched. The kinetics of the process of copper ion exchange on clinoptilolite under static conditions has been established.

Materials and Methods

Sufficient methods have been developed for the recovery of heavy metal ions from galvanic production waste water at present. The main disadvantages are mainly the high cost of the proposed sorbents, which increases the cost of waste water treatment technology.

The results of a number of researchers indicate a high selectivity of natural zeolites for the adsorption of ammonium ions [6, 7], heavy metals [8], radioactive elements [9]. An important feature of zeolites, and in particular clinoptilolite, is the ability to modify or activate their crystal structure by various methods [2, 10]: preheating or calcination; pre-chemical treatment with salts, acids or alkalis.

These methods allow to increase the specific content of zeolite as a result of dissolution or destruction of other non-zeolite impurities in the formation. In addition, they slightly expand the microstructure of the sorbent, thus increasing its porosity and specific surface area. But on the other hand, chemical treatment changes the crystal structure features of zeolite, which can contribute to the growth of ion exchange capacity by changing the cationic composition and creating new active centers.

The experiments were performed using chemical (volumetric) and physicochemical (gravimetric, photocolorimetric) methods of analysis. Investigations of the sorption properties of Sokyrnytsky clinoptilolite with a fraction of 0.5-1.0 mm were performed in a thermostated apparatus (constant operating temperature T = 20, 40 or 60ºC) under conditions of perfect mixing in batch mode. The content of copper or zinc ions in the filtered solutions was determined by standardized methods [11, 12].

The sorption values (cation exchange capacity E) of ions on clinoptilolite depending on the optimal ratio "solid : liquid" (S : L) were analyzed. To determine the amount of clinoptilolite of a certain mass (M = 2, 3, 4, 5, 6, 7, 10, 25, 50 g) it was treated with a model solution of copper sulfate with a concentration of $C_{0\ Cu}{}^{2+}$ = 10 g/dm^3 and a volume of 0.05 dm^3 during 2 hours. Under the selected experimental conditions the cation exchange capacity of the zeolite reaches maximum values under the condition S: L = 1: 10 (5 g: 0.05 dm^3).

During the first 10-20 minutes the intensive ion exchange takes place according to the obtained results (Fig. 1) on the establishment of kinetic features of the ratio of reagents in the system "solid - liquid" and the effect of temperature. Further the process slows down. This can be explained by the fact that the amount of active alkali metal ions in the clinoptilolite lattice capable of exchange decreases as the process progresses. Gradually, the equilibrium concentrations of exchange ions in the aqueous reagent medium (model solution) and in clinoptilolite are equalizing.

The maximum sorption capacity of clinoptilolite under selected conditions for different temperature regimes is achieved differently. For the temperature of the reagent medium T = 60 ºC the equilibrium occurs ~ at the 40th minute of the experiment, under the condition of the temperature T = 20 ÷ 40 ºC of the model solution - at the 60th minute. Analysis of the experimental curves allows us to establish that the highest sorption capacity of this mineral relative to copper ions is at a solution temperature T = 60 ºC.

This can be explained as follows. The pore entrances of clinoptilolite are limited by oxygen atoms, which are part of the tetrahedral complex. The frame structure of zeolite can not be considered absolutely rigid. This idea greatly simplifies the real state, because the electron density is distributed and therefore the effective radius of the entrance has no clear boundaries. Temperature affects the thermal fluctuations of the oxygen atoms of the entrance. According to [13] the standard deviation of atoms can reach 0.01-0.02 nm for room temperature. As the temperature increases, The effective radius of the entrance increases with the temperature rising, and the effective radius of the entrance decreases with the temperature decreasing. Therefore, given sufficient kinetic energy (temperature), sorbate penetrates into entrances better.

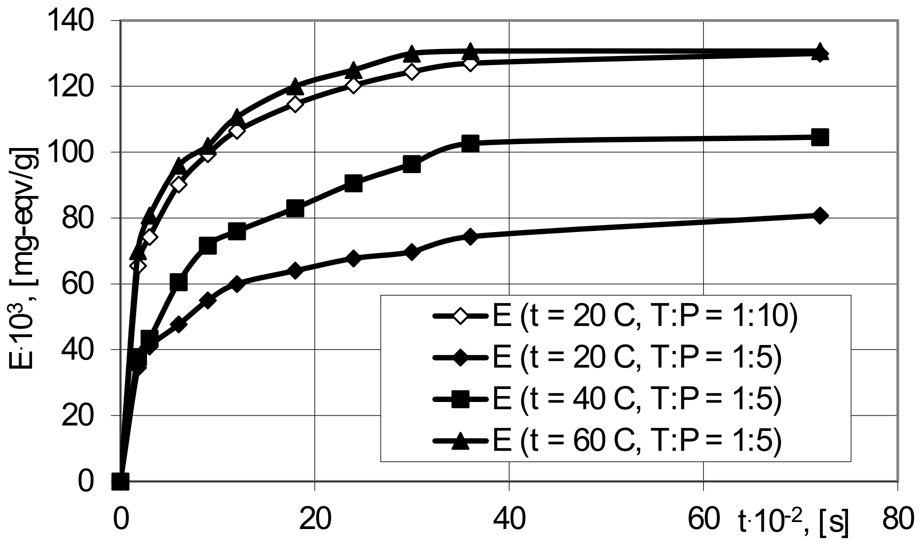

Fig. 1. The dependence of the ion exchange capacity of clinoptilolite E, mg-eqv / g on the treatment time t under static conditions at different temperatures and the ratio "solid - liquid"

The absorption of matter by the surface of macro- and mesopores takes place differently. This phenomenon is called "activated adsorption". However, the effect of temperature on the sorption of aqueous solutions is far from unambiguous. At the same time the physical sorption, like any exothermic process, generally deteriorates with increasing temperature. Therefore, the total manifestation of these two phenomena (activated and physical adsorption) is externally determined.

It is known from the literature sources [13, 14] that natural zeolites absorb cations from aqueous solutions by two mechanisms: cation exchange and adsorption. The increase in the concentration of hydrogen ions (or alkali and alkaline earth metals Na^+, K^+, Ca^{2+}, Mg^{2+}) in solution over time occurs due to purely ion exchange transformations. Thus, in terms of determining the mechanism of copper sorption by clinoptilolite, it is possible to assess the contribution of separate cation exchange and adsorption mechanisms in the total process of absorption of copper cations and $CuSO_4$ molecules by the mineral.

The natural and H^+ forms of clinoptilolite were used to set the mechanism of ion exchange. In both cases the pH medium changed sharply (for H^+-form of clinoptilolite – in the acidic region, for natural – in the alkaline) during the first 5 min and then gradually stabilized within an hour.

Determination of the SO_4^{2-}-anions content in the filtrate was performed according to standard methods [15] of the gravimetric method for determining the content of sulfate ions by binding and precipitation as an insoluble compound of barium sulfate, followed by calcination of sludge at T = 800 ºC in a muffle furnace for 2 hours, cooling in a desiccator and weighing. Indeed, if the absorption of copper by zeolite occurs by the mechanism of ion exchange, then with the absorption of copper ions into the solution the counter-ions (depending on the form of zeolite – ions of hydrogen or calcium, sodium, potassium) are transitted. And when the process is realized by the mechanism of physical adsorption, then the number of molecules of copper sulfate in the reagent medium should decrease. It was found that the adsorption process does not occur in this case - the number of bound SO_4^{2}- anions in all three cases remains unchanged.

In order to study the effect of chemical modification on the ion exchange capacity (E) of clinoptilolite relative to zinc and copper ions (see Fig. 2-4) the following acids, alkalis and salts (HCl, KOH, NaOH, KCl, NaCl) of different concentrations were used (0.1; 0.2; 0.4; 0.6; 0.8; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0 M).

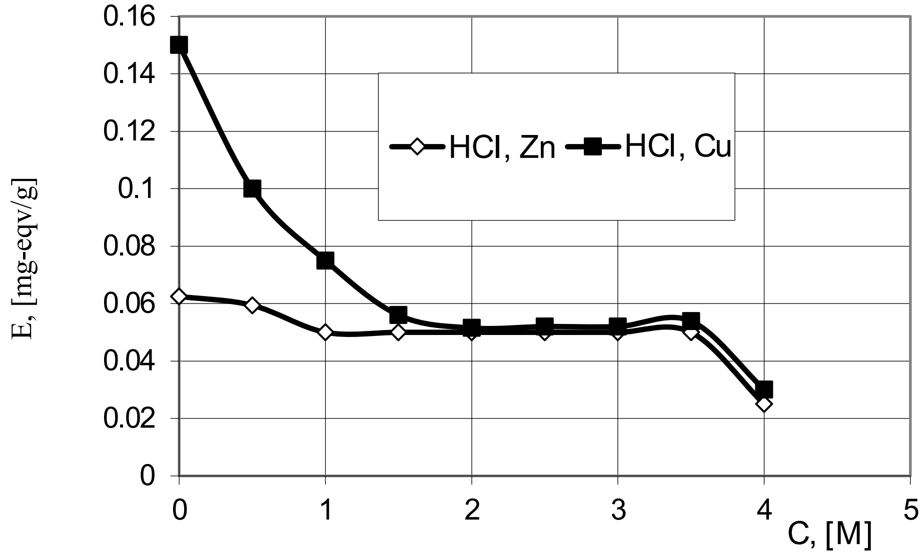

Fig. 2. Influence of modifier acid on the ion exchange capacity E of clinoptilolite relative to copper and zinc ions

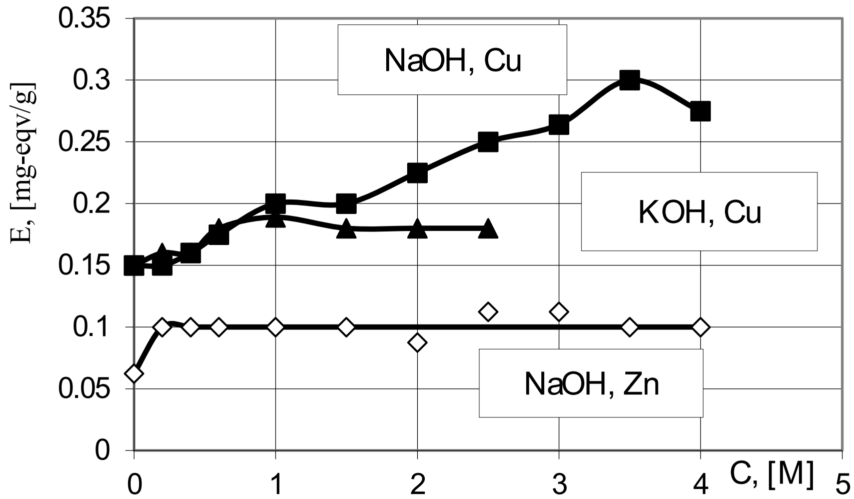

Fig. 3. Influence of modifier bases on the ion exchange capacity E of clinoptilolite relative to copper and zinc ions

According to our research it has been established that pre-modification with hydrochloric acid of different concentrations impairs the ion exchange properties of this mineral relative to copper and zinc ions. It can be seen that, after all, the amount of sorption space is not decisive for the ion exchange processes. It is known that fossil coal, which has virtually no developed pore system, shows a fairly high ability to sorb ions of many metals. Concentrated acid solutions destroy the crystal structure of clinoptilolite. The exchange cations and tetrahedral aluminum pass into the solution at the same time ("washed out") under the action of dilute acid solutions. Partial destruction of active exchange centers begins to occur, which causes a decrease in the ion exchange properties of zeolite. Some stability is observed in the hydrochloric acid concentration range C = 1.5 ÷ 3.5 M, although under such conditions aluminum ions are actively leached from the lattice. It is obvious that already for C = 4M HCl takes place the destruction of the framework (reduction of silicon ion content), zeolite begins to become more amorphous, the capacity relative to the cations of copper and zinc decreases again.

Treatment with alkalis NaOH and KOH under the same conditions showed (Fig. 3) a significant increase in the ion exchange capacity of clinoptilolite, although the concentrations were quite significant (C = 2 ÷ 4 M). The foundation is also a rigid modifier. Apparently in this case the samples of zeolite, pre-treated with alkalis, contained in their pores OH^-. Therefore, in the process of interaction with model solutions of copper sulfate the next reaction took place:

$$Cu^{2+} + 2OH^- = \underline{Cu(OH)_2}$$

Copper ions in the cavities turn into a hydroxide form and adsorbed as molecules by the developed surface of the mineral.

In addition, we have chosen sodium and potassium chlorides as a chemical modifiers. These metals are contained in the structure of clinoptilolite and are exchangeable. As expected (Fig. 4), treatment of mineral samples with alkali metal chlorides improves ion exchange capacity. Treatment with KCl salt did not lead to the desired changes.

This can be explained by the difference in the effective radii of the hydrated ions. Under the condition of pre-saturation with sodium ions, potassium, calcium and magnesium ions obviously pass into the solution, so the size of the entrance windows increases slightly. Otherwise, potassium ions slightly block the channels and as a result the sorption of copper cations is worse.

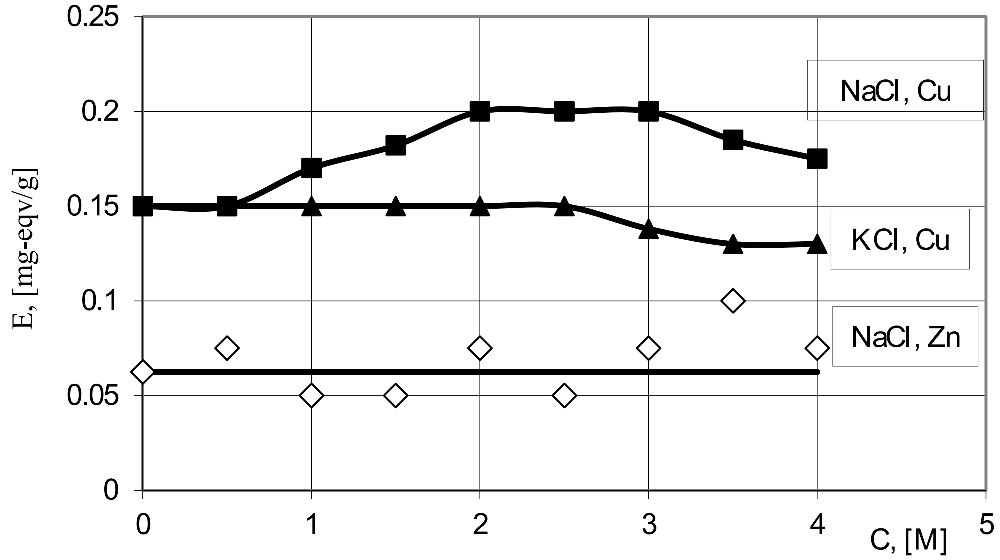

Fig. 4. Influence of modifying salts on the clinoptilolite ion exchange capacity relative to copper and zinc ions

An interesting feature is the much lower sorption capacity of clinoptilolite relative to zinc ions, given the similarity in size of the studied divalent cations. The authors [16] explain this discrepancy by the non-identity of the positions occupied by these cations in the clinoptilolite lattice. Copper ions are located in clinoptilolite at two types of sorption centers - cuboctahedra and in large cavities. In addition, by the chemical composition the cations Cu^{2+} are more likely to populate the shielded positions in the lattice than Zn^{2+} cations. As can be seen from the results of our experiments it is quite low on both natural and chemically modified forms of this type of zeolite. Therefore, ion-exchange clinoptilolite treatment of industrial waste water relative to zinc ions can be considered unpromising.

Thermal activation of rock. Literature sources show that the adsorption properties of natural zeolites depend on their primary heat treatment. Zeolites contain different types of water. According to [13] in the process of heating the zeolite to T = 105 ºC the hygroscopic moisture is released, up to 180 ºC – the crystal water, more than 350 ºC – zeolite water. The results of our research have shown that the ion exchange capacity of clinoptilolite decreases when calcined above T = 400 ºC. According to the results of X-ray diffraction analysis the crystal lattice begins to deform, aluminum-silicon-oxygen rings (entrance windows) are distorted, and possibly the number of active centers decreases. The colour of clinoptilolite changes from light gray-green to yellow-brick with increasing calcination temperature. This indicates that in the conditions of the experiments takes place a partial sintering of the most amorphous part of the mineral crystal lattice.

The sorption isotherm characterizes the statics of the process. After analyzing the data of literature sources for the construction of sorption isotherms we chose a range of concentrations of model solutions of copper sulfate solutions from a value 10 times higher than the MAC Cu^2 +, ie from 10 mg/dm^3 to the concentration of industrial waste water after copper baths – 30 g/dm^3 (10; 50; 75; 100; 250; 500; 750 mg/dm^3; 1; 5; 10; 20; 30 g/dm^3). The analysis of the filtrates was performed using a photocolorimeter according to standard method [11], preparing appropriate dilutions. The equilibrium cation exchange capacity of clinoptilolite was defined as the difference between the content in the initial and equilibrium concentrations of copper in the filtrate. Based on the obtained results the dependences were constructed - sorption isotherms $a = f(C)_T$, which are shown in Fig. 5.

Analysis of the nature of isotherms set for different temperature regimes once again confirms the effect of temperature on the ion exchange process on clinoptilolite - the higher the temperature, the better the ion exchange capacity relative to copper ions. As can be seen from Fig. 4, the sharp steepness of the isotherms indicates high selectivity for copper ions at low concentrations regions. Up to 0.5 g/dm^3 the mineral absorbs almost all copper ions from the model solution. The concentrations in the range of 0.75÷5 g/dm^3 is the transition region, and for higher concentrations the isotherms are gradually equalized.

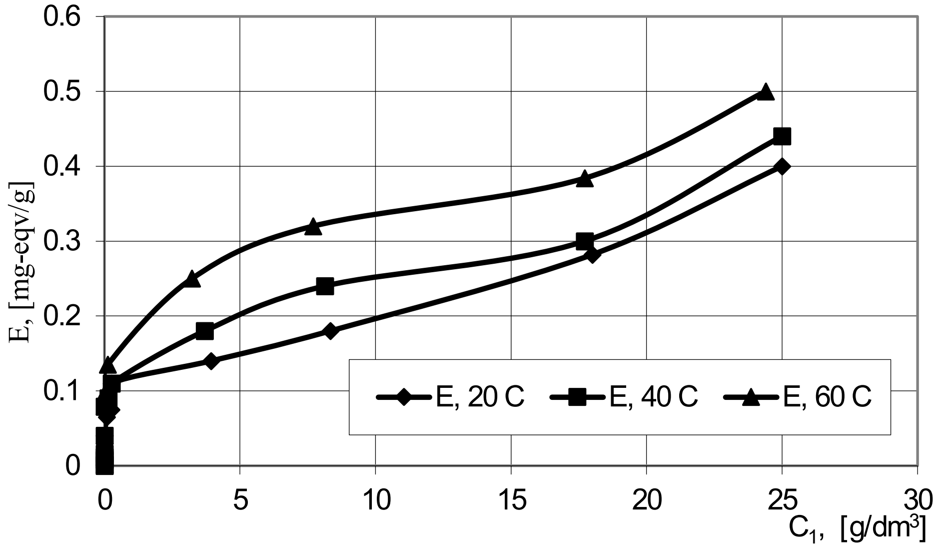

Fig. 5. Isotherms of sorption of copper ions by clinoptilolite for different temperature regimes (T = 20, 40 and 60º C). C1 – the equilibrium concentration, g/dm^3

Adsorption processes are usually satisfactorily described by Langmuir or Freundlich isotherms. That is, the process of saturation with a certain substance (gas, liquid) follows the following scheme: sorption increases to a certain maximum steepness, and then gradually equalizes until it becomes parallel to the abscissa. This means that all active centers are occupied. By the nature of the curves of the isotherm, in our opinion, can be attributed to the S-type isotherm. In addition, the steepness of the isotherms characterizes the size of the micropores of the sorbents. If the sorbent has a developed system of micropores and ultramicropores, the isotherm is more abrupt in nature. The flatness of the line indicates that the isotherm belongs to the transition - porous or macroporous sorbent.

The transfer of the substance in the porous body largely depends on the internal pore structure of the sorbent. Although theoretically clinoptilolite belongs to the framework type of zeolites with a uniform lattice structure, but in reality, of course, the pores of the body can form a slightly irregular, chaotic system. In addition, the mineral may contain up to 30% of impurities, which also complicate the process of ion exchange. Therefore, the explanation of this type of isotherm may be as follows. Copper ions move from the surface of the phases contact, where their concentration is high, to the depth of the pores to the active centers of exchange for alkali or alkaline earth metal ions. This continues until the state of equilibrium between the solution and the sorbent. Under the condition of increasing the initial concentration of the model solution, the equilibrium state, according to the Le Chatelier's principle, shifts to the right. Therefore, copper ions can occupy more difficult to access exchange positions. Accordingly, the exchange capacity of clinoptilolite (or the average concentration of adsorbed contaminants in the pores) increases.

Conclusion

Based on the above dependences, the process of the ion exchange sorption of copper by clinoptilolite will be best for the ratio of liquid and solid phases 1:10, elevated aqueous medium temperature. Ion-exchange treatment of industrial waste water from zinc ions by clinoptilolite is inefficient, so it is unpromising to plan the implementation of such a process on an industrial scale.

Purified water can be reused to wash parts after electroplating. Zeolite saturated with copper cations can be used as an inert catalyst carrier and as a microfertilizer with a prolonged action. Modification of clinoptilolite with the complexing agent Cu^{2+} increases the affinity of this zeolite to epichlorohydrin, which is contained in waste water from the production of glycerol and various epoxy resins, as well as to CO. In addition, the Cu^{2+}-form of clinoptilolite is actively used as a catalyst for hydrogenation-dehydrogenation reactions, cracking and other reactions in the field of organic synthesis. It is known that copper ions on the Cu^{2+}-form of clinoptilolite are able to intensify the exchange of skeletal oxygen to gaseous oxygen.

References

[1] D.V. Kulikova, O.S. Kovrov, Improvement of manufacturing scheme of wastewater treatment for galvanic shops of coal machine building enterprises. Ecological Safety and Balanced Use of Resources, **2(22)** (2021) 97-106.

[2] A. Zapolskyy, N. Mishkova-Klymenko, I. Astrelin, M. Bryk, Fizyko-Khimichni Osnovy Tekhnolohii Ochyshchennia Stichnykh Vod, Libra, Kyiv,2000.

[3] I.M. Chub, Masoobminni protsesy vodopidhotovky, KhNUMH im. O.M. Beketova, Kharkiv, 2020.

[4] O.I. Kuntyi, Halvanotekhnika, Vydavnytstvo Nats. Un-tu «Lvivska politekhnika», Lviv, 2004.

[5] T.V. Klymenko, Ochystka stochnykh vod ot yonov tiazhelykh metallov. Sovremennye nauchnye issledovanyia i innovatsii, **11** (2013).

[6] H. Sakalova, M. Malovanyy, T. Vasylinych, R. Kryklyvyi, The Research of Ammonium Concentrations in City Stocks and Further Sedimentation of Ion-Exchange Concentrate. Journal of Ecological Engineering, **20(1)** (2019) 158-164.

[7] V. Iurchenko, M. Radionov, O. Melnikova, O. Rachkovskiy, L. Mykhailova, Influence on Environmental Safety of the Drinking Water of Nitrification in Water Reservoir Being a Source of Water Supply and Filter Filling, Materials in Water Treatment Facilities. Materials Science Forum, **(1006 MSF)** (2020) 187-193.

[8] M. Malovanyy, H. Sakalova, T. Vasylinycz, O. Palamarchuk, J. Semchuk, Treatment of effluents from ions of heavy metals as display of environmentally responsible activity of modern businessman. Journal of Ecological Engineering, **20(4)** (2019) 167-176.

[9] M. Malovanyy, K. Petrushka, I. Petrushka, Improvement of Adsorption-Ion-Exchange Processes for Waste and Mine Water Purification. Chemistry & Chemical Technology, **13(3)** (2019) 372-376.

[10] S.S. Milovych, V.I. Homonai, A. Kovalchikova, Khimichnyi sklad i krystalichna struktura pryrodnoho klynoptylolitu Sokyrnytskoho rodovyshcha ta yoho modyfikovanykh form. Nauk. visnyk Uzhhorod. un-tu (Seriia Khimiia), **2(42)** (2019) 73-80.

[11] Yu.Iu. Lure, Unyfytsyrovannye metody analyza vod, Khimiia, Moskva, 1973.

[12] V.B. Aleskovskyi, V.V. Bardyn, M.Y. Bulatov, Fyzyko-khymycheskye metody analyza. Praktycheskoe rukovodstvo, Khimiia, Lenynhrad, 1988.

[13] D. Brek, Tseolytovyie molekuliarnyie syta, Mir, Moskva, 1976.

[14] M.D. Homelia, V.P. Ivanova, V.S. Kamaiev, Yu.A. Marushchak, Vyznachennia sorbtsiinoi zdatnosti ionitu pry vyluchenni ioniv midi z vody. Problemy vodopostachannia, vodovidvedennia ta hidravliky, **28** (2017) 84-91.

[15] A.S. Seheda, Analitychna khimiia. Kilkisnyi analiz, Fitosotsiotsentr, Kyiv, 2006.

[16] H.V. Sakalova, T.M. Vasylinych, Doslidzhennia efektyvnosti ochyshchennia stichnykh vod vid ioniv vazhkykh metaliv z vykorystanniam pryrodnykh adsorbentiv, TOV «Tvory»,Vinnytsia, 2019.

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Experimental Investigations of Removal of Phosphorus Compounds from Wastewater under Biological Purification

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Keywords: wastewater purification, phosphorus, immobilized microflora, aerobic conditions, anaerobic conditions, anoxic conditions, biological method.

Abstract. Today, most surface waters of Ukraine are eutrophied due to the entry into water bodies of a significant amount of nutrients – compounds of carbon, nitrogen and phosphorus.
Nitrogen and phosphorus enter water bodies with wastewater, sewage from agricultural lands and livestock farms, as well as with precipitation, due to the decomposition of water biomass, aquatic vegetation and zoocenoses. In the presence of free carbon dioxide (the concentration of which depends on bicarbonate alkalinity and water pH) and at certain rates of biochemical oxygen utilization (BOD) 7.2 g of nitrogen and 1 g of phosphorus produce 115 g of algae, which decomposition then consumes 115 g of oxygen [1]. BOD and dissolved oxygen are integral indicators that characterize ecological state of a water body on the whole. [2].

Introduction

The increase in the content of nitrogen and phosphorus compounds in water bodies occurs under the influence of both natural and anthropogenic factors.

Natural factors that affect the content of these elements in water reservoirs include their intake from the underlying soils, bottom sediments of water reservoirs, precipitation, etc. [3]. Eutrophication due to these processes is very slow, passes during thousands of years.

In contrast to natural ones, anthropogenic factors, the impact of which has been steadily increasing in recent years, leading to a rapid and sharp deterioration of water reservoirs [4]. Among them, such as inflows with local discharges of industrial [5], agricultural and domestic water (insufficiently purificated or without purification) [6, 7], and from dispersed sources (wastewater from agricultural land, surface wastewater from pastures and livestock farms, surface wastewater from settlements) [8].

In Ukraine and in the world, a lot of research is devoted to modeling and analysis of the content of dissolved oxygen in water and biochemical oxygen demand. In particular, rather substantive reviews are cited in publications [4, 9, 10].

One of the main ways that help solve problems related to the quality of surface waters, is mathematical modeling. After constructing a mathematical model of the dynamics of water quality, it is possible to determine the degree and depth of treatment, compliance with the standards of drinking water and commercial use [2].

Authors of [9, 11] proposed to determine the model parameters for a particular water site through solving classical equations. To enhance the accuracy of the model, other authors [12, 13] propose to introduce additional parameters to it or to analyze BOD of one and the same water sample in the double intervals of time [14]. A number of papers highlight the problems of modeling directly in management of water resources [15, 16].

Information on the amount of nitrogen and phosphorus compounds entering various water reservoirs from various sources is given in a range of works [17, 18].

That is why the removal of nitrogen and phosphorus is identified as one of the priority areas for improving wastewater purification technologies. Therefore, the purpose of this work is to develop wastewater purification technology from phosphorus compounds and bring their content to regulatory requirements.

Problem Formulation

Numerous studies have shown [17–22] that the use of immobilized attached microflora has a significant positive effect on the quality of treated water, reduces the number of purification plants and reduces the size of secondary settling tanks. However, these researches mostly studied the removal of organic compounds (COD and BOD) from wastewater and almost did not address issues that have recently become particularly important – the removal of phosphorus compounds from wastewater. Therefore, the possibility of using the attached microflora to reduce nitrogen and phosphorus concentrations in wastewater was studied in laboratory experiments. To study this issue in the laboratory two units were installed, which worked in parallel, using the same model solution. The obtained data of experimental researches allowed to develop technology of removal of phosphorus compounds simultaneously with biological sewage treatment.

Numerical Experiment

Two laboratory units were installed to conduct research on the removal of nitrogen compounds from wastewater. In the first unit, the conditions corresponding to the traditional biological purification system were simulated – an aeration tank with free-floating microflora (activated sludge) connected to a secondary settling tank. The activated sludge from the secondary settling tank was returned to the aeration tank by means of an airlift, the excess of which was removed from the unit through a pipe located in the lower part of the settling tank.

The second unit had an area in its upper part, which was filled with a carrier for fixing microorganisms on it. Polyurethane foam, previously tested in laboratory and industrial conditions for wastewater purification from organic compounds, was used as a carrier. Polyurethane foam due to porosity and high adsorption capacity is well overgrown with microorganisms. For many materials used as carriers for immobilization, the period of fouling, i.e. film coating of microorganisms, is 2-3 months. When using new polyurethane foam, the purification efficiency increases in 2-3 weeks, and when using polyurethane foam, which has been used before (for example, after repairing buildings), the cleaning effect is fully manifested in 3-5 days. The presence of pores in this material allows some microorganisms to penetrate into the middle, where there is a lack of oxygen and its concentration is not more than 1 mg / dm^3. That is, anoxide conditions are created in the internal pores, in which anaerobic microorganisms are optional. Therefore, polyurethane foam is overgrown with a multilayer culture, which combines both aerobic and anaerobic microorganisms. This allows you to combine aerobic and anaerobic processes in one unit.

The main advantage of using immobilized microflora [23, 24] in biological purification facilities is the ability to achieve significant, several times higher than in aerotanks with free-floating activated sludge, the concentration of microorganisms per volume unit of facilities. This is especially important when treating highly concentrated wastewater or when there is a bulk contamination.

An important advantage of immobilized microflora for wastewater purification, especially for phosphorus, is the elimination of the negative effects of reducing the load on activated sludge. According to the literature, as well as on the basis of studying the purification facilities of Chernihiv, for deep extraction of phosphates from urban wastewater, the load on sludge should be reduced against which the sedimentation properties of activated sludge are best (350-400 mg/g per day with BOD). But reducing the load on the sludge leads to an increase in the sludge index and the deterioration of its deposition. Therefore, during the operation of purification plants with a low load on activated sludge, the removal of activated sludge from secondary settling tanks and the deterioration of the quality of treated wastewater are usually observed, primarily in terms of "suspended solids". The use of microflora fixed on the carrier eliminates this disadvantage.

Immobilization of microorganisms on polyurethane foam carriers (Fig. 1) allows in case of unexpected arrival of significant concentrations of organic compounds or toxic compounds to save from death a significant proportion of activated sludge microorganisms and their rapid recovery, in contrast to traditional purification plants.

Fig. 1. Polyurethane foam

Taking the above into account, the unit was made in the form of cubes with a rib of 20 mm polyurethane foam based on polyesters of propylene oxide. This carrier has mainly open pores, the average diameter of which is from 0.4 to 1.8 mm, the average porosity is 97%.

Elastic polyurethane foams in such indicators as porosity, mechanical durability, hydrophobicity, adsorption properties have a significant advantage over many materials [25] used by carriers of activated sludge microorganisms.

There is evidence of reduced concentrations of nitrogen compounds when using polyurethane foam as a carrier. To carry out the denitrification process, the oxygen concentration in the installation must be reduced to 1.0-1.8 mg/dm^3.

The scheme of the experimental unit with parallel operating aeration tanks with fixed and free-floating activated sludge is shown in Fig. 2. Depending on the issues studied, the unit was supplemented with anaerobic or (and) anoxide zone.

The height of the columns, which ruled for aeration tanks, denitrifiers, settling tanks – 500 mm, the volume of water in aeration tanks – 4.5 liters, settling tanks – 1.5 liters. The residence time of water in the facilities was regulated by the consumption of water supplied for purification, which ranged from 0.4 to 1.5 dm^3/h, respectively, the residence time of water in the facilities for purification was from 3 to 10 hours, in settling tanks from 1 to 3.5 hours.

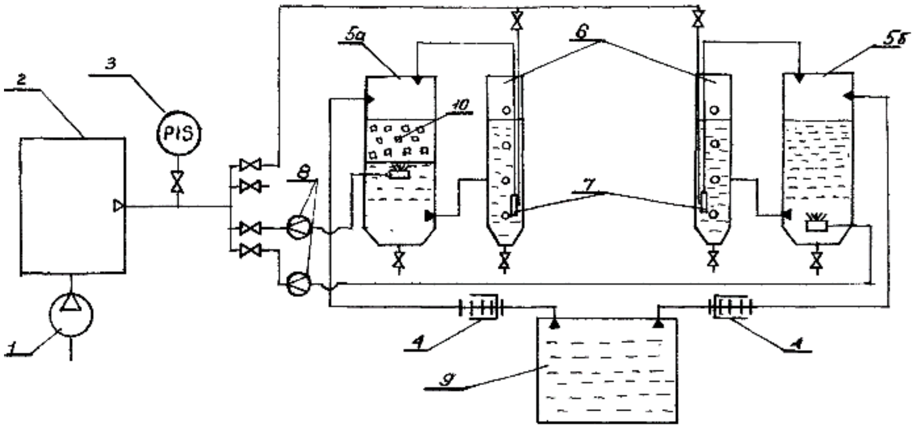

Fig. 2. Scheme of the experimental unit

1 - compressor, 2 - receiver, 3 - electrocontact manometer, 4 - piston pumps that supply model solutions into aeration tanks, 5 - aeration tanks (5a - with fixed activated sludge, 5b - with floating activated sludge), 6 - secondary settling tanks vertical, 7 - airlifts, 8 - rheometers that measure the flow of air supplied to aeration tanks, 9 - capacity for the preparation of model solution (or for source water), 10 - load for attaching activated sludge.

The air in the aeration tanks was supplied from the compressor through the receiver to maintain a constant pressure in front of the aeration tanks. The air in the aeration tanks was sprayed with the help of ceramic nozzles located at the bottom of the columns. Mixing of activated sludge in anaerobic and anoxide zones was carried out using a mechanical stirrer with a flexible shaft. Structurally, the flow of water from one reaction zone to another was performed using hoses that were connected to the fittings of the columns. This design allowed by changing the hoses to change the order of water passage in devices.

During the research, the unit worked 24 hours a day, in a continuous mode. After setting certain parameters for conducting experiments to adapt the microflora of activated sludge, the unit worked with the set parameters for 3 days, after which samples of source and purified water were taken, and the unit was adjusted to another desired mode. In the selected samples were determined those indicators that changed during the experiment and which during the process of biological purification: pH, COD, ammonium nitrogen, nitrites, nitrates, total phosphorus, phosphates. The following parameters as the concentration of activated sludge, the flow of water supplied into the unit, the flow of air, were also periodically monitored during the experiments. The water temperature was constantly maintained at the level of 18-22°C. After obtaining certain characteristics of the biological purification process, the unit was re-assembled in a series of experiments to study other issues.

Phosphorus removal under aerobic conditions

The study of phosphorus removal from wastewater was performed under aerobic conditions in an experimental unit at different modes and concentrations of pollutants. In the determination of phosphorus compounds, total phosphorus was also determined when using phosphorus-containing substances in the model solution as sources of organic compounds.

The results of the experiments are given in Table 1.

Table 1. Comparative analysis of phosphate removal during biological purification in units with immobilized and free-floating microflora

№	Output wastewater supplied into the unit		Water that passed through the unit with immobilized microflora		Water that passed through the unit with free-floating microflora	
	P_{gen} recalc. to PO_4^{3-}, [mg/dm³]	Phosphates PO_4^{3-}, [mg/dm³]	P_{gen} recalc. to PO_4^{3-}, [mg/dm³]	Phosphates PO_4^{3-}, [mg/dm³]	P_{gen} recalc. to PO_4^{3-}, [mg/dm³]	Phosphates PO_4^{3-}, [mg/dm³]
1	-	3.09	-	2.88	-	3.15
2	-	3.92	-	3.53	-	1.54
3	-	3.04	-	2.86	-	1.04
4	4.85	1.15	3.99	3.23	4.13	1.26
5	5.17	2.41	4.77	4.74	4.89	1.63
6	6.04	3.02	5.71	5.38	5.05	2.51
7	6.13	3.53	5.50	5.24	5.10	3.32
8	6.11	4.90	5.60	5.54	5.71	5.22
9	3.23	0.62	2.1	0.77	3.0	2.89
10	2.92	1.25	2.35	2.29	2.74	2.59
11	4.88	1.61	3.91	3.56	4.58	4.42
12	4.66	1.92	4.02	3.85	4.49	4.49
13	4.37	3.54	3.11	2.64	3.02	2.89

The obtained data indicate that in the biological purification of model wastewater there is destruction of organic phosphorus compounds with its transition to orthophosphates. At the same time there is a slight decrease in the concentration of total phosphorus, but its latter concentrations are quite high.

When using immobilized microflora, the reduction of phosphate concentration is somewhat higher than in the unit with free-floating microflora. This difference is not significant enough to assess the benefits of using immobilized microflora for wastewater purification from phosphorus compounds, as opposed to nitrogen compounds, where this difference is significant.

Of course, the anaerobic conditions created in the middle of the carrier to some extent improve the absorption of phosphates by microorganisms, but the ratio of aerobic zone and anaerobic zone in immobilized microflora is such that the aerobic zone is much larger than the anaerobic zone, where according to reference data the transition of phosphates back into aqueous solution takes place. Therefore, based on experiments on the removal of phosphates under aerobic conditions, we can conclude that the use of attached activated sludge in biological wastewater purification, although somewhat improves the conditions for removing phosphorus from wastewater, but due to deeper destruction of organic compounds containing phosphorus, its concentration remains high enough in wastewater.

Phosphorus removal under anaerobic conditions

To study this issue, a laboratory unit was installed in which anaerobic conditions were created and activated sludge was maintained in a suspended state by means of mechanical stirrers, as well as columns where anoxic conditions were maintained by feeding activated sludge from the settling tank by airlift. The activated sludge was also mixed with a stirrer. The ratio of activated sludge to wastewater flowing from the anaerobic zone was close to 1:1. The phosphate concentration was determined at the outlet of the settling tank. In addition, in separate experiments, wastewater with phosphates in the tank was mixed with activated sludge removed from the installation and stirred for 8 hours to determine the concentration of phosphates after each time.

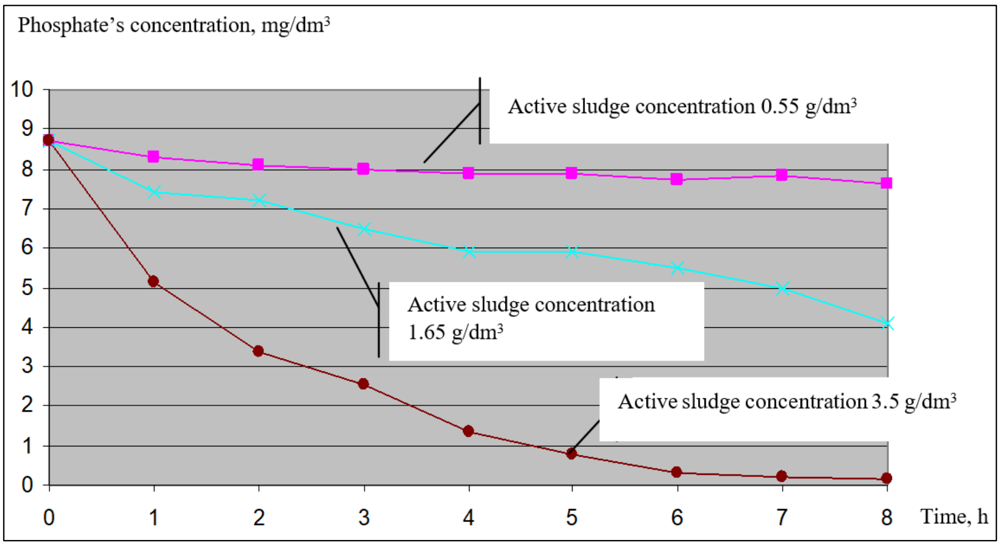

Fig. 3. Reducing the concentration of phosphates when mixing wastewater with activated sludge in conditions of limited access to oxygen

The results of experiments with activated sludge are given in Fig. 3. The concentration of organic compounds in the wastewater used was 380 mg/dm³ by COD.

Experimental data show that the level of phosphate removal under anaerobic conditions depends primarily on the concentration of activated sludge in contact with the phosphate solution (with wastewater). At a concentration of activated sludge of 3.5 g/dm³, the reduction of phosphates is vigorous, and after 8 hours of contact, the phosphate content is 0.18 mg/dm³. The oxygen concentration in the water at the beginning of the experiments was 1.5-2.0 mg/dm³, at the end of the experiments – 0.2-0.4 mg/dm³.

Thus, it is safe to say that under anaerobic conditions, with limited access to oxygen, phosphate removal proceeds to concentrations that are safe for discharge into water reservoirs.

During the operation of units supplied with anaerobic and anoxide blocks, the following results were obtained for the removal of phosphates from model wastewater, which are given in Table 2.

Table 2. Removal of phosphorus compounds when supplementing the experimental unit with anaerobic and anoxide zone

№	Output water		Purified water	
	COD, [mgO/dm³]	Phosphates, [mg/dm³]	COD, [mgO/dm³]	Phosphates, [mg/dm³]
1	754	31.42	107	5.82
2	384	20.4	44.3	1.17
3	312	21.5	31.4	1.91
4	284	12.9	20.8	0.32
5	463	15.4	37.1	0.21

Thus, the conducted experimental studies allow us to conclude that by providing conditions with limited access of oxygen to wastewater, it is possible to reduce the concentration of phosphates in wastewater that is reduced to a level that is safe for discharge into water reservoirs. The process of phosphate absorption takes place when the process is provided with organic food.

Technology of wastewater purification from nitrogen and phosphorus compounds in biological purification plants

When developing the technology, the following provisions were taken into account, which were obtained during experimental studies, and the general provisions of biological purification:

- removal of nitrate nitrogen requires anaerobic conditions and high concentrations of activated sludge;
- the transition of ammonium nitrogen to nitrates occurs under aerobic conditions, and the age of activated sludge should be at least 7-10 days;
- absorption of phosphorus by microorganisms occurs most fully in anoxic conditions, i.e. in the presence of oxygen in concentrations not exceeding 0.8-1.0 mg/dm^3;
- phosphorus absorption is negatively affected by the presence of nitrates, so their removal must precede the removal of phosphorus;
- the dose of activated sludge in the anaerobic zone should be 2-2.5 g/dm^3, in the aerobic zone - 2.503 g/dm^3;
- absorption of phosphorus by microorganisms of the fixed microflora requires less content of organic compounds than microorganisms of free-floating activated sludge;
- when removing nitrogen compounds in the anaerobic zone and phosphorus in the anoxide zone, the sludge index is higher than in traditional aerobic biological purification, so to prevent the removal of activated sludge from secondary settling tanks, it is desirable to use fixed activated sludge;
- the use of polyurethane foam as a carrier of fixed microflora provides partially anaerobic conditions in the depth of the carrier in the aeration zone (removal of ammonium nitrogen) and helps to reduce the concentration of nitrates in the anoxide zone and, accordingly, promotes better phosphate absorption;
- the technology of removal of nitrogen and phosphorus compounds, taking into account the above, is as follows.

Wastewater containing organic compounds, phosphates and mainly ammonia nitrogen enters the anaerobic zone, which returns the activated sludge from the secondary settling tank after the aerobic zone with water containing nitrates, and in this zone partially returns water from the anoxic zone with active sludge to reduce the age of activated sludge in the anaerobic zone. In the anaerobic zone, nitrates from surface activated sludge are reduced to molecular nitrogen. Water that does not contain nitrates and is partially purified from organic compounds (during denitrification) then enters the anoxide zone, which is also fed water with activated sludge from the aeration zone, thus ensuring a minimum concentration of oxygen in the anoxide zone. In this zone, the absorption of phosphates from water in an amount exceeding the needs of microorganisms to build cellular material.

From the anoxide zone, the water together with the activated sludge enters the aeration zone, where the final purification of wastewater from organic compounds and ammonium nitrogen, which is oxidized to nitrates. From this zone, the sludge water partially returns to the anoxide zone. After the aerobic zone, the purified water with sludge enters the secondary settling tanks, where the sludge is separated from the water and mainly returned to the anaerobic zone, and part of it in the form of excess sludge is removed from purification plants. As this sludge contains 2-2.5 times more phosphates than traditional activated sludge, it can be used as a valuable fertilizer for agriculture after dehydration and composting.

To keep the activated sludge in the anaerobic zone in a suspended state, mechanical stirrers are installed in it. The peculiarity of their work is that they should not capture air during operation.

To increase the efficiency of phosphorus removal and reduce the residence time of wastewater in the aeration zone polyurethane foam in the form of cubes with a rib size of 20 mm is placed in the aeration zone. In the place of water flow from the aeration tank to the secondary settling tank, a grid with a mesh size of 7x7 mm is installed to hold the polyurethane foam cubes and prevent its removal to the secondary settling tank.

Thanks to the pump that supplies circulating water to the anoxide zone, the polyurethane foam also moves to this zone. Therefore, the carrier load of the immobilized microflora is distributed between the anoxide and aeration zone and circulates between them. In order to prevent damage to the pieces of foam, the pump installed to dispense water from the aeration to the anoxide zone must be low-speed and have a large gap between the impeller and the housing.

The scheme of the developed and recommended technology of wastewater purification from nitrogen and phosphorus compounds at biological purification facilities shown in Fig. 4 demonstrated experimental studies for 85-95%.

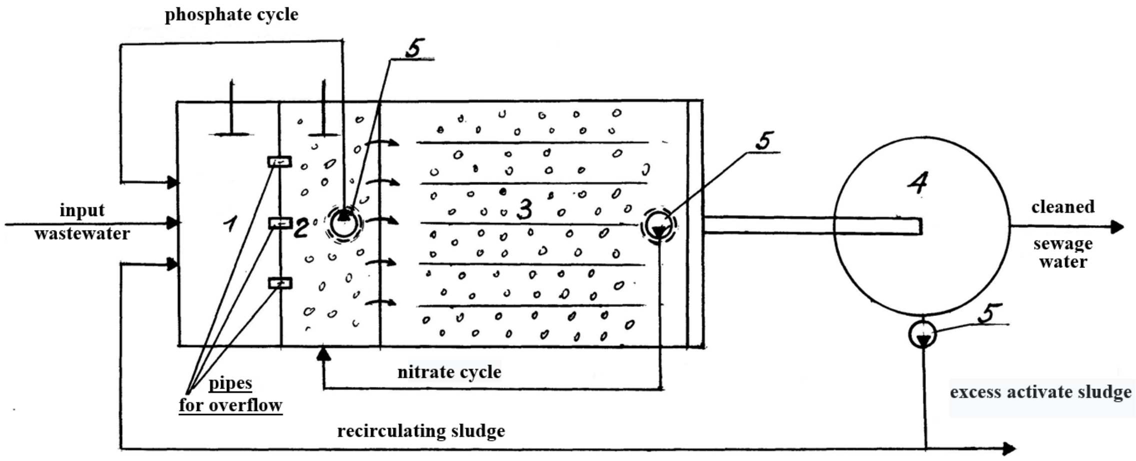

Fig. 4. Schematic diagram of wastewater purification containing organic pollutants from nitrogen and phosphorus in biological purification plants: 1 - anaerobic zone, 2 - anoxide zone, 3 - aeration zone, 4 - secondary settling tank, 5 - circulating pumps

This scheme allows the simultaneous removal of wastewater from organic compounds and suspended solids in purification facilities with traditional technology to ensure the removal of nitrogen and phosphorus compounds, as

Process parameters are defined as follows:

- concentration of activated sludge in the anaerobic zone - 2.0-2.5 mg/dm^3;
- concentration of activated sludge in anoxide and aeration zones - 2.5-3.0 mg/dm^3;
- consumption of circulating activated sludge from the primary settling tank in the anaerobic zone - 100-110% of the consumption of wastewater;
- consumption of circulating activated sludge between the aeration zone and the anoxide zone - 120-150% of the consumption of wastewater;
- consumption of circulating activated sludge between the anoxide and anaerobic zone - 80-100% of the consumption of wastewater;
- the residence time of water in each zone is determined by the concentration of pollutants in the source wastewater;

- activated sludge load on organic compounds - 250-300 g/g day for $BOD_{complete}$;
- load on the surface of secondary settling tanks - 0.8-1.0 $m^3/m^2 \cdot h$.

Conclusion

Thus, on the basis of our own experimental research, taking into account world experience [26], a technology for removing nitrogen and phosphorus compounds was developed simultaneously with biological wastewater purification. The main conditions for the efficiency of this technology are the mandatory presence in wastewater of organic compounds, defined as $BOD_{complete}$, in the ratio of total phosphorus 30:1, in the case of use of facilities with free-floating activated sludge. In the case of use of biological purification facilities with fixed microflora, this ratio changes to 7-10:1. Therefore, the use of fixed microflora allows to effectively remove phosphorus from wastewater with less organic matter, which expands the range of wastewater that can be purified from phosphorus by biological method.

References

[1] I.M. Andrusyshyna, "Beware of phosphates". Voda i vodoochisnye tekhnologii, 5(65) (2012)4–9.

[2] Bezsonnyi V., Tretyakov O., Khalmuradov B., Ponomarenko R. Examining the dynamics and modeling of oxygen regime of chervonooskil water reservoir. Eastern-European Journal of Enterprise Technologies, 5 (2017) 32–38.

[3] N.I. Podorvan, L.I. Globa, N.I. Kulikov, and P.I. Gvozdyak, "Removal of phosphorus compounds from waste water". Himiya i tehnologiya vodyi, 6(26) (2004) 591–610. [in Ukrainian].

[4] Loboichenko V., Strelec V. The natural waters and aqueous solutions express-identification as element of determination of possible emergency situation. Water and Energy International, 61 (9) (2018) 43–50.

[5] Pospelov B., Rybka E., Meleshchenko R., Borodych P., Gornostal S. Development of the method for rapid detection of hazardous atmospheric pollution of cities with the help of recurrence measures. Eastern-European Journal of Enterprise Technologies, 1 (10–97) (2019) 29–35.

[6] Danchenko Y., Andronov V., Kariev A., Lebedev V., Rybka E., Meleshchenko R., Yavorska D. Research into surface properties of disperse fillers based on plant raw materials. Eastern-European Journal of Enterprise Technologies, 5 (12–89) (2017) 20–26.

[7] Loboichenko V., Strelets V., Leonova N., Malko A., Llyinskiy O. Comparative analysis of anthropogenic impact on surface waters in Kharkiv region. Indian Journal of Environmental Protection, 40 (2) (2020) 134–139.

[8] K. Tsytlishvili, A. Matsak, O. Rybalova, S. Artemiev, A. Romin, O. Chynchyk, Method of agricultural sewage water purification at troughs and a biosorption bioreactor. Eastern-European Journal of Enterprise Technologies, 5 (10) (2018) 15–24.

[9] A. Vasyukov, V. Loboichenko, S. Bushtec, Identification of bottled natural waters by using direct conductometry. Ecology, Environment and Conservation, 22 3 (2016) 1171–1176.

[10] B. Pospelov, E. Rybka, R. Meleshchenko, S. Gornostal, S. Shcherbak, Results of experimental research into correlations between hazardous factors of ignition of materials in premises. Eastern-European Journal of Enterprise Technologies, 6 10 90 (2017) 50–56.

[11] Popov O., Iatsyshyn A., Kovach V., Artemchuk V., Taraduda D., Sobyna V., Sokolov D., Dement M., Hurkovskyi V., Nikolaiev K., Yatsyshyn T., Dimitriieva D. Physical features of pollutants spread in the air during the emergency at NPPs. Nuclear and Radiation Safety, 4 (84) (2019) 11.

[12] Loboichenko V., Andronov V., Strelec V. Evaluation of the metrological characteristics of Natural and treated waters with stable salt composition identification method. Indian Journal of Environmental Protection, 38 (9) (2018) 724–732.

[13] Vasenko A., Rybalova O., Kozlovskaya O. A study of significant factors affecting the quality of water in the Oskil River (Ukraine). Eastern-European Journal of Enterprise Technologies, 3 (10–81) (2016) 48–55.

[14] Loboichenko, V., Leonova, N., Shevchenko, R., Kapustnik, A., Yeremenko, S., Pruskyi, A. Assessment of the impact of natural and anthropogenic factors on the state of water objects in urbanized and non-urbanized areas in lozova district (Ukraine). Ecological Engineering and Environmental Technology, 22 (2) (2021) 59-66.

[15] Rybalova O., Artemiev S., Sarapina M., Tsymbal B., Bakhareva A., Shestopalov O., Filenko O. Development of methods for estimating the environmental risk of degradation of the surface water state. Eastern-European Journal of Enterprise Technologies, 2 (10–92) (2018) 4–17.

[16] Loboichenko V., Vasyukov A., Tishakova T. Investigations of Mineralization of Water Bodies on the Example of River Waters of Ukraine. Asian Journal of Water, Environment and Pollution, 14 (4) (2017) 37–41.

[17] V. M. Loboichenko, A. E. Vasyukov, T. S. Tishakova, Investigations of mineralization of water bodies on the example of river waters of Ukraine. Asian Journal of water, environment and pollution, 14(4) (2017). 37–41. [in Ukrainian].

[18] L.A. Sabliy, Physico-chemical and biological purification of highly concentrated waste waters: Monograph. Rivne: NUVGP, 2013. 292 p. [in Ukrainian].

[19] S.C.S. Martins, C.M. Martins, L.M. Cidrão Guedes, S.T. Fiúza Santaella, Immobilization of microbial cells: A promising tool for treatment of toxic pollutants in industrial wastewater. African Journal of Biotechnology, 12(28) (2013) 4412–4418.

[20] M. Blyashyna, Process of biological wastewater treatment for nitrogen, phosphorus removal by immobilized microorganisms. Eastern-European Journal of Enterprise Technologies, 2/10 (92) (2018) 30–37.

[21] Lee Ch.-H., Lee S.-K., Lee K., Lee S.H., Choi D.-Ch. Container with biofilm formationinhibiting microorganisms immobilized thereon and membrane water treatment apparatus using the same. US 2016/0030890 A1, Pub. Date: Feb. 4, 2016.

[22] J.-P. Hernandez, L.E. de-Bashan, Y. Bashan, Starvation enhances phosphorus removal from wastewater by the microalga Chlorella spp. co-immobilized with Azospirillum brasilense Hernandez. Enzyme and Microbial Technology. 38 (2006) 190–198.

[23] M.V. Blyashina, L.A. Sabliy, Technology and possession for anaerobic-aerobic purification of sewage waters. Materials of the exhibition and conference "Cooperation to solve the problem of waste", (2012).

[24] IURCHENKO Valentyna, TSYTLISHVILI Kateryna, MALOVANYY Myroslav, Wastewater treatment by conversion of nitrogen-containing pollution by immobilized microbiocenosis in a biodisk installation. *Ecological Questions* [online], 33 (2) (2022) 1–17.

[25] D. Yelatontsev, A. Ivanchenko, O. Kryukovska, Research and mathematical description of the effect of temperature on the kinetics of phosphates and suspended solids extraction from wastewater. Environmental safety. Bulletin of the KrNU named after Mikhail Ostrogradsky, 2(97) 1 (2016) 70 – 75.

[26] A.P. Sincero, G.A. Sincero, Physical–chemical treatment of water and wastewater, CRC Press LLC, (2003), Florida, USA.

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Research of Modern technologies of Wastewater Treatment of Food Products Combined with Ozonation and Hydrogen Peroxide

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Keywords: food industry, wastewater treatment, biodisks reactor, Advanced Oxidation Processes (AOPs), oxidants, ozone, hydrogen peroxide.

Abstract. The paper presents studies of the process of purification of model wastewater, which contained high concentrations of animal proteins, fats and hydrocarbons. The model wastewater solution was treated by biosorption treatment in a bioreactor; with pre-ozonation (O_3) and biosorption purification in the bioreactor and in the variant with pre-treatment with ozonation and hydrogen peroxide – by the method of AOPs (O_3/H_2O_2) or the process «Peroxon». The efficiency of cleaning by chemical oxygen consumption when using the AOPs method reached (97-98) %, disinfection – up to 100 %.

Problem Formulation

One of the promising areas for wastewater treatment and disinfection is the use of natural oxidants such as oxygen, ozone and hydrogen peroxide. Combining these methods – Advanced Oxidation Processes (AOPs) has a synergistic effect, resulting in deep oxidation of substances [1], which are contained in wastewater from food production and are difficult to decompose.

The problem of ensuring the proper ecological status of water resources remains relevant for all regions of Ukraine [2, 3]. Miscellaneous conditions and factors influencing the for-mation of groundwater quality predetermine the need to study the factors that have the biggest impact. Studies in this area are topical due the fact that contemporary climate changes and an intensive use of water resources require identifying the largest sources of pollution of surface waters for further development of a complex of environment protection measures [4, 5]. Virtually all surface and a significant part of groundwater resources [6, 7], especially in areas of powerful industrial, including food production are experiencing anthropogenic impact, manifested in pollution, depletion and degradation of these objects [8, 9]. Traditionally, the "main" pollutants are industrial enterprises [10, 11]. Chemical pollution of the atmosphere on a global scale leads to acid rain [12] and the greenhouse effect, which significantly impairs water quality [13].

Wastewater from the food industry is highly concentrated and multicomponent, which includes organic and inorganic substances. The traditional destructive method of treatment is a biochemical method in which the treatment of oxidation of substances (including toxic) in wastewater [14]. Some proteins as well as fats and synthetic surfactants (SS) are difficult to biochemically decompose, which creates difficulties during biological treatment. Therefore, traditional methods of treatment of such wastewater cannot provide an adequate level of treatment.

Improve the quality of wastewater treatment, which can be achieved by treating it with strong oxidants, such as ozone, ultraviolet radiation, hydrogen peroxide. Using them in different combinations increases the efficiency of the wastewater treatment process.

Biochemical oxygen demand and dissolved oxygen are integral indicators that characterize ecological state of a water body on the whole [15]. In modern wastewater treatment technology there is a tendency to use environmentally «friendly», natural oxidants, such as air oxygen, ozone, oxygen, hydrogen peroxide, ultraviolet radiation. The use of these oxidants does not lead to secondary contamination of water by their decomposition products, which does not have a harmful effect during the discharge of treated water into the surface water body or in the case of its further safe use.

Analysis of Publications

The paper [16, 17, 18] analyzes the state of a number of bodies of surface water of the Kharkiv region (Ukraine), which are under various types of anthropogenic impact. Total dissolved solids (TDS) and conductivity indicators are used as parameters of comparison.

The research paper [19] contains the analysis of surface and groundwaters quality evaluation approaches. It has been stated that the initial stage of waters identification can be carried out with the help of one or a range of criteria. Known identification approaches are expensive, time consuming or require an immense amount of data. Natural and treated waters with stable salt composition identification method based on the initial water electrical conductivity as well as the identification coefficient measurement are suggested to use.

The paper [20] presents the procedure for assessing the risk of disturbance of the water body. The procedure is based on determining the environmental standards of surface water quality, taking into account the landscape and geographical features of river basins. A database of surface water monitoring systems was used to assess the risk of deterioration of the aquatic ecosystem.

The issues of building a mathematical model to determine the approximate required level of reduction of harmful effects on the surface water body (site) for the inflow of pollutants are considered by the authors [21].

Research on wastewater treatment is of practical interest. The activation of coagulant solutions and their use for technical water purification are investigated in the work [22]. Studies [23] show that in the ozonation of pre-settled and filtered wastewater, the oxidation of dissolved organic matter is most intense in the first 20-30 minutes, and the speed and depth of the ozonation process increases sharply with increasing sewage pH and ozone concentration. It has been experimentally established that it is necessary to treat wastewater at a pH not lower than 6.5, which is expedient both from a technological and economic point of view.

The optimal parameters of the process of ozonation of domestic wastewater are proposed: pH 8-8.5, ozone concentration 50-55 mg/dm^3, exposure – 20-30 minutes [24]. The authors proved that the oxidizing properties of ozone are most pronounced in an alkaline environment. At pH 11-12, ozone consumption 450-550 mg/dm^3, the intensity of coloration of domestic wastewater is reduced by 20-25 times, the amount of suspended solids is reduced by 15 times [25].

The description of the method and the most complex laboratory equipment for the study of the quality of biological wastewater treatment is presented in [26].

Aim of Paper

The aim of the work is to determine the optimal conditions of purification and additional treatment of model wastewater in a bioreactor with pre-treatment by the method of AOPs for highly concentrated wastewater from food production.

Materials and Methods

In the experimental study used a model solution, which is a whey from milk, which was diluted with stagnant tap water in a ratio of 1:10. The model solution was in a reactor 1.2 m high. Hydrogen peroxide solution (1.5 cm^3/dm^3 liquid) was added to the reactor and purged with ozone-air mixture with ozone concentration – 5 mgO_3/dm^3 at ozone dose – 1 g/m^3 (O_3/H_2O_2 = 1 g: 0.5 g). The treatment took place within 7.1 minutes. Next, the treated water was added to a biosorption reactor of the aerotank-mixer type [27], where the oxidation of pollutants by the biocenosis immobilized on the reactor disks took place (Fig. 1). The process was monitored by pH, dissolved oxygen concentration and chemical oxygen demand (COD).

Fig. 1. Installation of combined wastewater treatment compatible with ozonation and hydrogen peroxide and biosorption method

Concentrations of ozone and hydrogen peroxide for experimental studies are selected depending on the type of pollutants and their initial concentration.

When determining the parameters of model runoff treatment by immobilized biocenosis in a biodisks reactor with pre-treatment of ozonation runoff (volume of waste liquid in the finished form – 10 dm^3, where the water level in the column – 80 cm) at the bottom of the column immersed spray tube ozone-air mixture for bubbling.

Initial data for the experiment: the dose of ozone in the mixture – 5 mg/dm^3; consumption of O_3 in the mixture – 1 l/min.; the concentration of O_3 in the ozone-air mixture is 7 mg/dm^3.

Model runoff processing period 7 minutes 8 sec. At the end of this period, the treated wastewater in a volume of 10 dm^3 was drained and defended for 5-7 minutes. and poured into the bioreactor for further purification with immobilized activated sludge. Control of ozonation and biotreatment was performed by pH, dissolved oxygen concentration and chemical oxygen demand (COD). After ozonation treatment, the wastewater was sent to a bioreactor.

When determining the parameters of model runoff treatment by immobilized biocenosis in a biodisk reactor with pre-treatment with ozonation and hydrogen peroxide (AOPs-method), a nebulizer tube was placed on the bottom of the column through which ozone-air mixture was fed hydrogen drip.

Initial data for the experiment: the fixed dose of ozone in the mixture was 5 mg/dm^3; consumption of O_3 in the mixture – 1 dm^3/min.; concentration of O_3 in the ozone-air mixture – 7 mg/dm^3; the period of treatment of the model wastewater is 7 minutes 10 sec.; dose of hydrogen peroxide 0.5 g per 1 g of O_3, i.e. 3.5 mg of H_2O_2 in 1 min.

Based on this, the calculation of the dose of H_2O_2 was introduced: from 35 % solution of perhydrol (H_2O_2) was dissolved in 200 ml of water and obtained 0.175%, or 0.175 g/100 g of water (1.75 g/l or 1.75 mg/ml).

The rate of dripping is 2 ml/min, ie 3.5 mg of H_2O_2 in 1 min, and O_3 is 7 mg/dm^3. Thus, the ratio of H_2O_2: O_3 = 3.5: 7 = 0.5: 1.

The cost of hydrogen peroxide at a dosage of 2 ml/min. During the period of ozonation of the model solution for oxidation spent hydrogen peroxide 15 ml of 0.175 % H_2O_2.

At the end of this period, the treated model solution in a volume of 10 dm^3 was drained and defended for 5-7 minutes. and poured into the bioreactor for further purification with immobilized activated sludge.

Purification was performed under the following conditions at the optimal mesophilic temperature: T air – 22 ^0C; T water – 21 ^0C [28]. According to the scientific literature, the optimal content for the oxidation of only organic matter is 1.0-1.5 mg/dm^3 [29], 3.5-4.0 mg/dm^3 [30].

Research Results

The optimal formation of hydroxyl radicals in combined wastewater treatment with ozonation and hydrogen peroxide (AOPs-method) or in the Peroxone process depends on the ratio of H_2O_2/O_3, pH, ozone concentration, contact time, composition of the aqueous phase of the wastewater. Excess hydrogen peroxide is undesirable due to its interaction with hydroxyl radicals. When hydrogen peroxide decomposes in a chain reaction, secondary hydroxyl radicals are formed, which accelerates the oxidation process and makes it more efficient. The combined method of water treatment is most effective in the phased dosing of hydrogen peroxide.

The process of «Peroxon» is based on a combination of two powerful oxidants of hydrogen peroxide with ozone, which interact to form hydroxyl radicals and active oxygen according to the scheme: $H_2O_2 + 2O_3 \rightarrow 2OH^{-} + 3O_2$

It was noted that the immobilized biocenosis on disks differed in color and density along the receiving bath along the course of wastewater. This is due to the fact that saturated with oxygen and organic matter wastewater is treated in a bioavailable form for the microflora, mainly heterotrophs. The purification process is more intensive due to the fact that the water is additionally saturated with oxygen during rotation. Due to this synergy, a rapid decrease in the concentration of organic matter in the COD was found.

Table 1 shows the parameters of the treatment of model runoff by ozonation, followed by additional purification by biosorption method.

Table 1. Parameters of modeling effluent treatment by ozonation followed by purification by biosorption method

Indicators	0 h (untreated runoff)	After ozonation	1 h	2 h	3 h	4 h	5 h
O_2 concentration, [mg/dm^3]	3.70	4.18	4.01	4.6	4.3	4.2	4.8
pH	6.18	6.14	7.2	7.35	7.5	7.55	7.68
COD, [mgO/dm^3]	1260	1215	805 (34%)	644 (49%)	491 (61%)	274 (78%)	120 (90%)

The data in Table 1 show that after treatment of the liquid with ozone, the value of HSC decreased slightly, but after 2 hours of treatment in the bioreactor HSC decreased by more than 60 % from the initial COD of wastewater and amounted to 491 mg/dm^3. And after 4 hours the cleaning effect reaches almost 90 %, which is equal to the cleaning effect of the biosorption method.

Table 1 shows the parameters of purification of the model solution by ozonation and hydrogen peroxide (process «Peroxon»), followed by additional purification by biosorption method.

Table 2. Parameters of purification of model solution by ozonation and hydrogen peroxide (Peroxon process) with the subsequent purification by biosorption method

Indicators	0 h (untreated runoff)	After ozonation + H_2O_2	1 h	2 h	3 h	4 h	5 h
O_2 concentration, [mg/dm^3]	4.58	4.48 (column); 4.41 (glass)	4.35	4.35	4.26	4.40	4.4
pH	5.8	5.85	7.24	7.34	7.26	7.32	7.38
COD, [mgO/dm^3]	1425	925 (35 %)	508 (64 %)	468 (67 %)	263 (81,5 %)	159 (89 %)	74 (95 %)

After treatment with ozone-air mixture in combination with hydrogen peroxide oxidation, the COD of the model solution decreased by almost 35 % and reached 925 mgO/dm^3. The model runoff with the following characteristics was added for purification in a biosorption disk reactor with immobilized biocenosis. And within an hour of treatment in the biodisks reactor COD decreased by 64 %, but also significantly increased the pH value by almost 2 units. The results of purification of the model solution by biosorption method with pre-treatment with ozonation and hydrogen peroxide are presented in Table 2. The table shows that under the influence of powerful oxidants complex chemicals that are part of whey decompose. This is observed in the reduction of COD at a rate of 420 mgO/dm^2 in the first hour of treatment, and after the second hour the rate decreases significantly, probably due to residual concentrations of organic matter and on average this rate is 90 mgO/dm^2. The pH value after the first hour of treatment remains approximately the same value. Wastewater with this value of medium can be directed to sewage networks for modular biological treatment plants.

Thus, purification of model wastewater by biosorption method in a biodisks reactor after pre-treatment with ozone-air mixture together with hydrogen peroxide allowed to reduce the time in the treatment system to 2.5-3 hours and achieve the effect of COD treatment to 95 %.

Comparative analysis of the results of treatment of model wastewater by different methods is given in Table 3.

Table 3. Dynamics of COD (mg/dm^3) model runoff during its treatment by different methods

Options of processing of a model drain	Initial COD	COD after processing O_3	COD after processing O_3/H_2O_2	Dynamics of COD in the bioreactor				
				Processing period in the bioreactor, [hour]				
				1	2	3	4	5
In the bioreactor	1389	–	–	1100	816	370	218	168
				Cleansing effect, [%]				
				21	41	73	84	88
With pre-treatment O_3	1260	1215	–	805	681	644	274	120
		Cleansing effect, [%]						
		4	–	36	46	49	78	90
With pre-treatment O_3/H_2O_2	1425	–	925	508	468	263	160	74
			Cleansing effect, [%]					
			35	64	67	82	89	95

Thus, pre-ozonation combined with the addition of hydrogen peroxide allows you to more effectively purify water that contains high concentrations of substances that are difficult to biodegradable. The dynamics of decomposition of organic matter by COD model wastewater during treatment by different methods is presented in the graph (Fig. 2).

Table 3 and Figure 2 show that the period of oxidation of pollutants in the model solution after treatment with ozonation in conjunction with hydrogen peroxide was reduced by 2 hours compared to previous treatment with ozone. The purification effect for 3 hours was 82 %, which is almost equal to the effect after 5 hours with pre-treatment only with ozone with an effect of 90 %. The highest effect of removal of organic matter by COD by the method of AOPs was 95 %.

Thus, pre-treatment with the AOPs method of the model solution contributed to the oxidation of sparingly soluble substances, which reduced the COD of the model runoff by 64 % after 1 hour of treatment in a biodisks reactor.

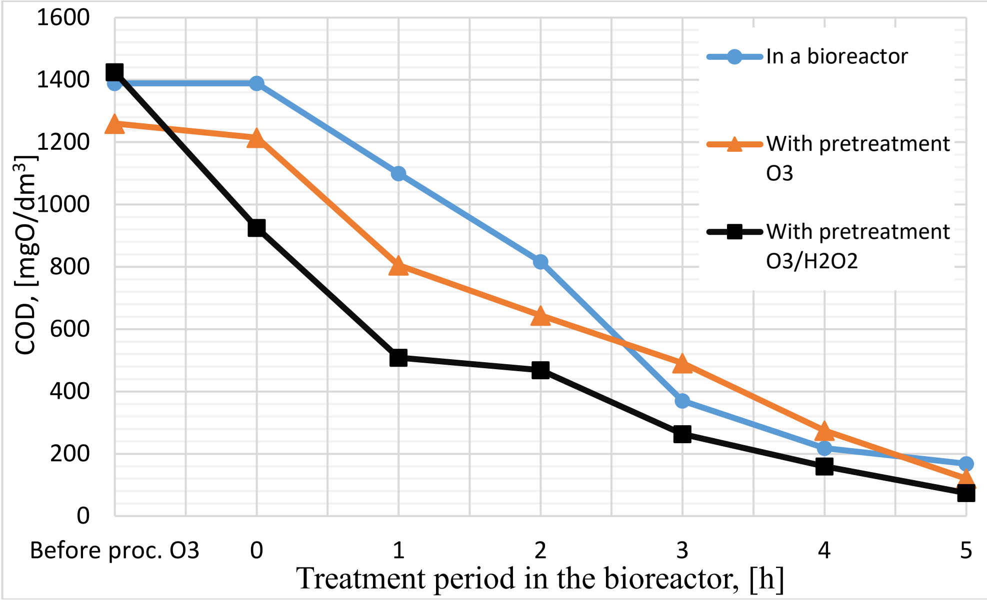

Fig. 2. Dynamics of COD model wastewater during treatment by different methods

1 – biosorption treatment in a biodisks reactor;

2 – biosorption treatment in a biodisks reactor with pre-treatment with ozone (O_3): A – COD before treatment with O_3; B – COD after O_3 treatment, which is the initial for biosorption purification in a biodisks reactor;

3 – biosorption treatment in a biodisks reactor with pre-treatment by the method of AOPs: A' – COD before treatment by the method of AOPs; B' – COD after treatment of AOPs, which is the initial for biosorption purification in a biodisks reactor.

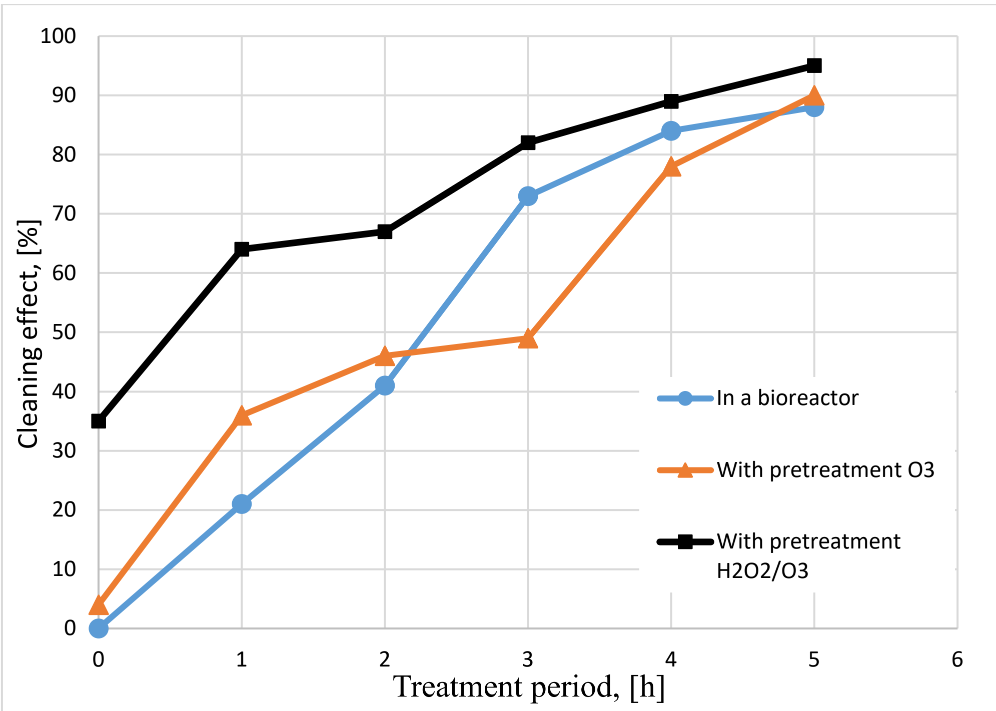

Fig. 3. Dependence of the effect of purification of the model solution on the treatment period

1 – biosorption treatment in the bioreactor;

2 – biosorption treatment in a bioreactor with pre-ozonation (O_3);

3 – biosorption purification in the bioreactor with pre-treatment by AOPs (O_3/H_2O_2).

Table 4 presents the results of measuring the rate of oxidation of organic pollutants depending on the method of purification.

Table 4. The rate of oxidation reactions of the model runoff in the bioreactor

Options of processing of model drain	COD initial [mg/dm^3]	Processing period, [hour]				
		1	2	3	4	5
		Oxidation rate (ΔCOD, [mg/dm^3 : t, hour]), [mg/dm^3/hour]				
In the bioreactor	1389	289	286.5	340	293	244
In the bioreactor with pre-treatment O_3	1215	410	286	285	219	178
In the bioreactor with pre-treatment O_3/H_2O_2	925	420	229	221	191	170

Table 4 shows that the rate of oxidation of organic matter by COD after 2 hours of treatment in all three variants almost coincide. But it is noted that with pre-treatment in the first hour destructive processes occur almost 2 times faster and reach 410-417 mg/dm^3 per hour.

To determine the effect of the AOPs method (O_3/H_2O_2) on the treatment efficiency, the model runoff was treated at the same initial COD values separately by the biosorption method and the AOPs method (O_3/H_2O_2).

The prepared drain was added to a column 1 m 20 cm high. The drain volume is 10 l. (water level in the column – 80 cm).

At the bottom of the column was placed a spray through which the model drain was fed ozone-air mixture and a dispenser mounted on it through which hydrogen peroxide was added.

At the end of the treatment period, the model solution in a volume of 10 dm^3 was drained and defended for 5-7 minutes. and poured into the bioreactor for further purification with immobilized activated sludge.

In the biodisks reactor, the solution was treated under contact conditions at a disk rotation speed of 14 rpm Table 5 shows that a rapid decrease in organic matter by COD is observed after 2 hours, more than 2 times with a total purification effect of 88 %. In the Table 5 provides parameters for the treatment of highly concentrated effluent in the bioreactor.

Table 5. Dynamics of wastewater treatment in a bioreactor

Indicators	Before cleaning	1 h	2 h	3 h	4 h	5 h	Cleaning effect, [%]
COD, [mgO/dm^3]	1389	1100	816	370	218	168	88

The cleaning effect was 88 %.

In the Table 6 presents the results of treatment of highly concentrated effluent by biosorption method, but with pre-treatment by AOPs and subsequent purification by ozonation and O_3/H_2O_2.

Table 6. Dynamics of purification and purification of model effluent in a bioreactor with pre-treatment by AOPs (O_3/H_2O_2)

Indicators	Output	AOPs treatment	Further purification in the bioreactor					O_3 purification	AOPs purification
			1 h	2 h	3 h	4 h	5 h		
O_2, [mg/dm^3]	3.30	3.48	3.40	3.73	4.04	3.65	3.41	4.16	4.4
pH	6.13	6.11	6.25	6.12	6.07	5.92	5.41	5.68	5.77
COD, [mgO/dm^3]	1320	1180	890	644	580	315	90	83	78

As a result, it was found that the effect of sewage treatment by biosorption (with pre-treatment of AOPs) – 92 %, and the effect of treatment as a whole (with pre-treatment of AOPs) – 96 %, additional treatment by AOPs reduced COD by another 13 %. At COD, treated wastewater can be discharged into a surface water body.

Fig. 4 shows the dependence of the process of model runoff treatment on the treatment period in the case of the AOPs method.

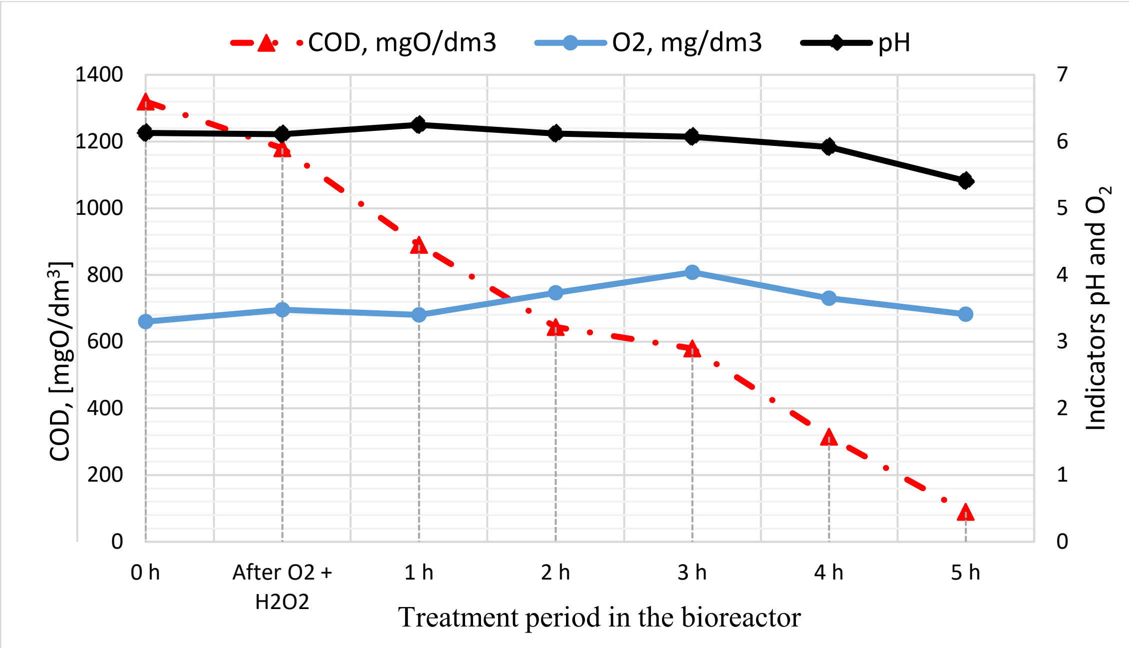

Fig. 4. Dynamics of indicators in the treatment of runoff in the bioreactor in the case of pre-treatment by the method of AOPs

From the experimental data it was found that after treatment of the effluent by the method of AOPs (7 min. 10 s.) COD effluent decreased by 11 %.

Further purification of this model wastewater solution in the bioreactor reduced the COD by 96%.

Purification of wastewater by ozonation (within 10 minutes) allowed to reduce COD by 7 %; and parallel purification by the AOPs method (within 10 minutes) allowed to reduce the COD by 13 % and achieve such COD values at which the discharge of runoff into the surface water body is allowed.

Conclusions

The efficiency of model effluent treatment by model effluent treatment in a bioreactor pre-treated with AOPs (O_3/H_2O_2) is slightly higher than after O_3 treatment, namely by 5.5 % with an initial organic matter content of 860 mgO/dm^3 higher. Thus, as a result of experimental studies, the optimal conditions for purification and purification of the model wastewater solution in the bioreactor with pre-treatment by the method of AOPs for highly concentrated wastewater production.

Establishing optimal concentrations of hydrogen peroxide and ozone at which on the one hand the oxidation of substances that are difficult to decompose and on the other hand prevent the addition of excess hydrogen peroxide due to its interaction with hydroxyl radicals.

The basic technological scheme of wastewater treatment of food industry enterprises is developed, which is based on the combination of physico-chemical method of wastewater treatment with biosorption treatment and AOPs method.

It is established that, when combining physico-chemical method of wastewater treatment with biosorption treatment and AOPs method, deep wastewater treatment is achieved to indicators that meet the normative values set for: discharge into surface water, municipal treatment facilities or use for technical purposes enterprises.

References

[1] O. Vasenko, I. Zinchenko, K. Tsytlishvili, V. Bikaso. Research of methods of inactivation of the antibiotic cyprofloxacin in order to prevent environmental pollution and protect human health. Scientific Horizons, 7 (2020) 19–25.

[2] V.M. Loboichenko, A.E. Vasyukov, T.S. Tishakova. Investigations of mineralization of water bodies on the example of river waters of ukraine. Asian Journal of water, environment and pollution, 14(4) (2017) 37–41.

[3] Loboichenko, V., Leonova, N., Shevchenko, R., Kapustnik, A., Yeremenko, S., Pruskyi, A. Assessment of the impact of natural and anthropogenic factors on the state of water objects in urbanized and non-urbanized areas in lozova district (Ukraine). Ecological Engineering and Environmental Technology, 22 (2) (2021) 59-66.

[4] Popov O., Iatsyshyn A., Kovach V., Artemchuk V., Taraduda D., Sobyna V., Sokolov D., Dement M., Hurkovskyi V., Nikolaiev K., Yatsyshyn T., Dimitriieva D. Physical features of pollutants spread in the air during the emergency at NPPs. Nuclear and Radiation Safety, 4 (84) (2019) 11.

[5] Dubinin, D., Avetisyan, V., Ostapov, K., Shevchenko, S., Hovalenkov, S., Beliuchenko, D.,Maksymov, A., Cherkashyn, O. Investigation of the effect of carbon monoxide on people in case of fire in a building [Article@Ispitivanje djelovanja ugljičnog monoksida na ljude u slučaju požara u zgradi] Sigurnost, 62 (4) (2020) 347-357.

[6] O. Rybalova, S. Artemiev, M. Sarapina, B. Tsymbal, A. Bakhareva, O. Shestopalov, O. Filenko. Development of methods for estimating the environmental risk of degradation of the surface water state. Eastern-European Journal of Enterprise Technologies, 2(10–92) (2018) 4–17.

[7] Loboichenko V., Strelec V. The natural waters and aqueous solutions express-identification as element of determination of possible emergency situation. Water and Energy International, 61RNI (9) (2018) 43–50.

[8] Natsional′na dopovid′ pro stan navkolyshn′oho pryrodnoho seredovyshcha v Ukrayini u 2014 rotsi. K.: Ministerstvo ekolohiyi ta pryrodnykh resursiv Ukrayiny, FOP Hrin′ D.S. 350, 2016 [in Ukraine].

[9] B. Pospelov, V. Andronov, E. Rybka, O. Krainiukov, K. Karpets, O. Pirohov, I. Semenyshyna, R. Kapitan, A. Promska, O. Horbov, Development of the correlation method for operative detection of recurrent states. Eastern-European Journal of Enterprise, 6/4 102 (2019) 39–46.

[10] B. Pospelov, E. Rybka, R. Meleshchenko, P. Borodych, S. Gornostal, Development of the method for rapid detection of hazardous atmospheric pollution of cities with the help of recurrence measures. Eastern-European Journal of Enterprise, 1/10 97 (2019) 29–35.

[11] V. Sadkovyi, B. Pospelov, V. Andronov, E. Rybka, O. Krainiukov, A. Rud, K. Karpets, Yu. Bezuhla, Construction of a method for detecting arbitrary hazard pollutants in the atmospheric air based on the structural function of the current pollutant concentrations. Eastern-European Journal of Enterprise, 6/10 108 (2020) 14–22.

[12] M. Kustov, V. Kalugin, V. Tutunik, E. Tarakhno, Physicochemical principles of the technology of modified pyrotechnic compositions to reduce the chemical pollution of the atmosphere. Voprosy khimii i khimicheskoi tekhnologii, 1 (2019) 92–99.

[13] A. Vasyukov, V. Loboichenko, S. Bushtec, Identification of bottled natural waters by using direct conductometry. Ecology, Environment and Conservation, 22 3 (2016) 1171–1176.

[14] A. Matsak, K. Tsytlishvili, O. Rybalova. Method of agricultural sewage water purification at troughsand a biosorption bioreactor. Eastern-European Journal of Enterprise Technologies, 5(10-95) (2018)16–25.

[15] Bezsonnyi V., Tretyakov O., Khalmuradov B., Ponomarenko R. Examining the dynamics and modeling of oxygen regime of chervonooskil water reservoir. Eastern-European Journal of Enterprise Technologies, 5 (10–89) (2017) 32–38.

[16] V. Loboichenko, V. Strelets, N. Leonova, A. Malko, O. Ilyinskiy, Comparative analysis of anthropogenic impact on surface waters in Kharkiv region. Indian Journal of Environmental Protection. 40(2) (2020) 134–139.

[17] Loboichenko V., Tishakova T., Vasyukov A. Application of direct coulometry for rapid assessment of water quality in Krasno-Oskol Reservoir (Kharkiv Region, Ukraine). Der Pharma Chemica, 8 (19) (2016) 27–34.

[18] Loboichenko, V., Andronov, V., Strelets, V., Oliinykov, O., Romaniak, M. Study of the State of Water Bodies Located within Kharkiv City (Ukraine). Asian Journal of Water, Environment and Pollution, 17 (2) (2020) 15-21.

[19] Loboichenko V., Andronov V., Strelec V. Evaluation of the metrological characteristics of Natural and treated waters with stable salt composition identification method. Indian Journal of Environmental Protection, 38 (9) (2018) 724–732/

[20] Rybalova O., Artemiev S. Development of a procedure for assessing the environmental risk of the surface water status deterioration. Eastern-European Journal of Enterprise Technologies, 5 (10–89) (2017) 67–76.

[21] R. Ponomarenko, L. Plyatsuk, L. Hurets, D. Polkovnychenko, N. Grigorenko, M. Sherstiuk, O. Miakaiev. Determining the effect of anthropogenic loading on the environmental state of a surface source of water supply. Eastern-European Journal of Enterprise Technologies, 5 10(105) (2020) 54–62.

[22] Dushkin S., Galkina O. More Effective Clarification of Circulating Water at Coke Plants. Coke and Chemistry, 62 (10) (2019) 474–480.

[23] V.P. Sidenko, A.I. Prikazyuk Gigiyenicheskoye obosnovaniye ispol'zovaniya ozona v prirodookhrannoy tekhnologii ochistki i obezzarazhivani zagryaznennykh vod na transporte. Aktual'nyye problemy transportnoy meditsiny, 4(10) (2007) 42–52 [in Russian].

[24] R.R. Munter Problemy tekhnologicheskogo oformleniya protsessov ozonirovaniya stochnykh vod. Tez. VII Vsesoyuznogo simpoziuma po sovremennym problemam prognozirovaniya, kontrolya kachestva vody vodoyemov i ozonirovaniya. Tallin, (1985) 3–13 [in Russian].

[25] O.M. Ivan′ko, L.I. Bidnenko Suchasni metody znezarazhennya stichnykh vod (ohlyad literatury). Ukrayins′ka viys′kovo-medychna akademiya. Kharkiv. (2012) 137–150 [in Ukrainian].

[26] Sposib doslidzhennya yakosti biolohichnoho ochyshchennya stichnykh vod z vykorystannyam kompleksnoho laboratornoho ustatkuvanny : pat. 142646 Ukrayina : MPK (2006.01) S02F 3/02. № u 2019 10647; zayavl. 28.10.2019 ; opubl. 25.06.2020, Byul. № 12 [in Ukrainian].

[27] IURCHENKO Valentyna, TSYTLISHVILI Kateryna, MALOVANYY Myroslav, Wastewater treatment by conversion of nitrogen-containing pollution by immobilized microbiocenosis in a biodisk installation. *Ecological Questions* [online], 33 (2) (2022) 1–17.

[28] Metodika provedeniya tekhnologicheskogo kontrolya raboty sooruzheniy po ochistke stochnykh vod utverzhdena prikazom Predsedatelya Agentstva RK po delam stroitel'stva i zhilishchno-kommunal'nogo khozyaystva ot 29.11.2011 № 539 [in Russian].

[29] O.V. Khar'kina Effektivnaya ekspluatatsiya i raschet sooruzheniy biologicheskoy ochistki stochnykh vod. Volgograd : Panorama, 2015, 433 p.

[30] A.A. Slovtsov Sovershenstvovaniye protsessov biologicheskoy ochistki stochnykh vod s pomoshch'yu prikreplennykh biotsenozov. Vestnik MGSU. 3 (2008) 83–85 [in Russian].

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Electrochemical Formation of Aluminum Coagulants for Dairy Wastewater Treatment

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Keywords: dairy wastewater; coagulant; electrocoagulation; degree of purification; mechanism of coagulation action

Abstract. Researches of chemical-technological parameters of electrochemical production of aluminum-based coagulants for electrocoagulation wastewater treatment of milk processing enterprises have been carried out. The impact of pH and the timing of the electrocoagulation process was studied in two cases of the implementation of the technological process: with the addition of an alkaline additive before and after the electrocoagulation treatment. The mechanism of the coagulation action of aluminum compounds formed as a result of electrocoagulation has been studied. It has been established that the addition of an alkaline additive after electrocoagulation is more effective. At the same time, the degree of wastewater treatment remains quite high. This will ensure energy savings and will positively affect the environmental and economic assessment of the technology.

Introduction

Factories and enterprises for the production of dairy food products are the source of the most dangerous wastewater, which in case of irrational and irresponsible use can significantly affect the state of surface and underground natural reservoirs. In addition, the ingress of these waters without prior treatment or treatment for treatment at urban treatment plants can cause disruption of biological treatment systems and the death of activated sludge [1-4].

Wastewater from dairy plants is a complex heterogeneous system that is a mixture of ionic and molecular solutions, suspensions, emulsions and colloidal solutions (sols). The dispersion medium is water, and the dispersed phase is represented by solid inorganic particles emulsified by insoluble fat droplets, particles of coagulated protein, organic acids, lactose, and colloidal particles of organic contaminants [1, 5, 6].

It is known that for the primary treatment of dairy wastewater are the most effective chemical methods or treatment with chemical reagents electrolytes – sulfates, chlorides, hydroxy salts of aluminum or iron, calcium chloride, etc. Crystal salts of metals, entering the water, dissolve, hydrate, dissociate and hydrolyze with the formation of colloidal particles of insoluble hydroxides of metals – coagulants. Charged colloidal hydroxide particles are characterized by excess surface energy and increased adsorption capacity, which allows you to effectively remove both dispersed and dissolved contaminants in wastewater [7]. The addition of salts provides not only the removal of major contaminants – fats, proteins, organic acids, lactose, suspended solids, but also nutrients – compounds of nitrogen and phosphorus, chlorides, sulfates, etc. [8-10]. The disadvantages of the chemical method of obtaining coagulants are the need for additional equipment for storage and dosing of chemical reagents, secondary contamination of wastewater with sulfates, chlorides, etc.

A more ecological and economical way to obtain coagulants – metal hydroxides, is electrochemical dissolution of metal (aluminum, iron, copper, zinc, etc.) anodes in electrolyte solutions, which is successfully used in electrocoagulation method of wastewater treatment of different chemical composition [11-15].

Literature Review

When using metal anodes, electrolytic dissolution occurs with the transition to a solution of metal ions, which subsequently form coagulants - insoluble metal hydroxides. Newly formed coagulants have increased adsorption activity to colloidal and suspended particles and are used in the processes of electrocoagulation of wastewater treatment. During electrocoagulation of wastewater, other electrochemical, physicochemical and chemical processes can take place in the following sequence: electrophoretic concentration (directed movement of dispersions as freely charged particles and their concentration near the electrode surface); electrolytic dissolution of anodes and formation of metal hydroxides; polarization coagulation of dispersed particles; packaging of primary units and flocculation coagulation; flotation of the formed aggregates by bubbles of electrolytic gases. All these processes in the complex provide a high degree of purification of contaminated wastewater, which are in different phase-dispersed states.

The process of electrochemical formation of coagulants is influenced by many factors: the material of dissolved anodes, the number of anodes in the cell, pH, current, the presence of other electrolytes in wastewater, voltage, duration of electrocoagulation, etc. [11, 12, 14-16]. The efficiency of electrocoagulation is usually assessed by the degree of wastewater treatment from a particular type of pollution, which is characterized by a certain indicator. For example, for dairy wastewater, these indicators may be chemical oxygen demand (COD), the amount of ethereal soluble substances (ESS), the amount of suspended solids, etc.

In [11], electrocoagulation of dairy wastewater was performed using aluminum electrodes and the efficiency of the process was evaluated by the value of COD and the amount of suspended solids. It was found that at the initial pH≈5 of wastewater, at an electric current density of 61.6 A/m^2, which was applied for 21 minutes, COD decreased by 57% and the total amount of suspended solids decreased by 97%. At the same time, the pH of treated (treated) wastewater increased to 10.

Electrocoagulation of palm oil production wastewater was studied in [16]. It was found that the optimal number of aluminum electrodes for maximum treatment of wastewater from dyes is 4, the optimal voltage is 15 V. The amount of added electrolyte NaCl for maximum efficiency of the treatment process is 1.67 g/dm^3.

In [17], the authors investigated the electrocoagulation treatment of wastewater from a paper processing plant. The efficiency of the process was determined by the following indicators of wastewater: chemical oxygen demand (COD), the amount of suspended solids, the amount of ammonia and color. To increase the efficiency of pollutant removal, a combination of four vertically arranged electrodes was used in the electrolyzer, in which two iron electrodes were located between two aluminum electrodes. The influence of the duration of the electrocoagulation process, electric voltage and initial pH of wastewater on the efficiency of wastewater treatment from the above pollutants is determined. It is established that the optimal parameters of electrocoagulation are the value of electric voltage 10 V, the initial pH of wastewater 7, the duration of the process – 60 minutes. Under these conditions, the removal efficiency of COD, suspended solids, color and ammonia is 79.5%, 83.4%, 98.5% and 85.3%, respectively.

The authors [18] conducted experiments on electrocoagulation of wastewater treatment of acetic acid production. The arrangement of the laboratory installation consisted of three vertically arranged aluminum and three iron electrodes, three of which were the cathode and three - the anode. The comparative characteristics of two cases were studied: aluminum electrodes - anodes and iron electrodes - anodes. The cathodes, respectively, were iron or aluminum electrodes. According to the technology, additional chemical reagents were added to wastewater - sodium sulfate to increase electrical conductivity, as well as high molecular weight polymeric substances of organic and inorganic nature to improve the coagulation process. The influence of electric current density, pH value and nature of the additive on the efficiency of the wastewater electrocoagulation process was studied. It was found that in the case of aluminum anodes, current density 20 mA/cm^2 and initial pH4, 90.91% of COD removal was achieved. At the same time, 42.42 kWh/m^3 of electricity was used for processing. It is established that in the case of using iron anodes, current density

22.5 mA/cm^2, initial pH~9, without any chemical additives, the removal of COD reaches 93.58%. 47.06 kWh/m^3 of electricity was used for processing.

Many scientific studies have studied the patterns of electrochemical formation of coagulants [18-22]. The main chemical reactions of aluminum hydroxide formation that occur in the process of electrocoagulation of wastewater are the following (in the case of aluminum anodes):

- on aluminum anodes of aluminum oxidation:

$$Al_{(solid)} \rightarrow Al^{3+}_{(aqua)} + 3e; \quad (1)$$

- on the cathodes of water reduction:

$$3H_2O + 3e \rightarrow 3/2\ H_{2\ (gas)} \uparrow + 3OH^-_{(aqua)}; \quad (2)$$

- formation of coagulant in acidic or neutral environment:

$$Al^{3+}_{(aqua)} + 3H_2O \rightarrow Al(OH)_{3(solid)} \downarrow + 3H^+_{(aqua)}; \quad (3)$$

- formation of coagulant in alkaline medium:

$$Al^{3+}_{(aqua)} + 3OH^-_{(aqua)} \rightarrow Al(OH)_{3(solid)} \downarrow. \quad (4)$$

According to the authors [12, 16, 19-21], in an alkaline environment monomeric are formed $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$ and polymer $Al_2(OH)_2^{4+}$, $Al_2(OH)_5^+$, $Al_6(OH)_{15}^{3+}$, $Al_{13}(OH)_{34}^{5+}$ aluminum complexes, which are able to increase the efficiency of electrocoagulation due to the fact that they have both positive and negative charges. However, experimental data [18, 22] show that increasing the initial pH value of wastewater can, conversely, reduce the efficiency of electrocoagulation. According to the authors [18], at pH>7 a gel layer is formed on the aluminum anode, which slows down the oxidation processes and, accordingly, the formation of coagulant.

Thus, it is established that the efficiency of electrochemical formation and chemical nature of coagulants (metal hydroxides, complex ions) for electrocoagulation treatment of dairy wastewater directly depends on the conditions of the process. First of all, the pH of the source wastewater, the presence of various pollutants, the strength or density of the electric current, the duration of the experiment. The mechanism of coagulant formation in media with different pH values has been found to be incompletely studied, especially the electrochemical formation of aluminum-based coagulants. Therefore, the study of chemical and technological parameters of electrochemical production of coagulants based on aluminum for electrocoagulation wastewater treatment of dairy enterprises is an important scientific and practical task.

Materials and Methods of Research

Wastewater from a dairy plant in the Sumy region (Ukraine) was used for the study. For research during two working shifts, wastewater samples were taken from the milk collection area, laboratory, cheese shop, hardware department, butter shop, processed cheese shop and sales department. Taking into account the contribution to the total runoff of each section of the enterprise, the total runoff with the average composition of wastewater was formed.

Electrocoagulation treatment of wastewater was carried out in a laboratory installation, which includes an electrolyzer made of organic glass with dimensions of 18 cm × 15 cm × 4 cm. The volume of treated wastewater was about 1 dm^3. The area of aluminum electrodes was about 250 cm^3. Sodium hydroxide NaOH in the form of a 5% aqueous solution was used as an alkaline additive.

The efficiency of treatment was studied by the following indicators of wastewater: pH, transparency, amount of ether-soluble substances, content of orthophosphate ions PO_4^{3-} and ammonium nitrogen ions NH_4^+ [2, 23]. The pH was determined at a temperature of 18-20^{0}C using a portable pH meter brand SX 711 (China) with a measurement accuracy of ± 0.001pH. The transparency of the water was determined using a Snellen instrument, which is a glass cylinder with a flat bottom. The amount of essential soluble substances (fats and mineral oils) (ESS) was determined by the method of multiple extraction with petroleum ether as an extractant. After evaporation of the ether from the extract by weight, the mass of all soluble ether-soluble substances was determined. The content of orthophosphate ions and ammonium nitrogen ions was determined by photometric method using a laboratory photometer.

Discussion of the Research Results

To study the effect of pH on the patterns of coagulant formation and treatment efficiency, wastewater with an average composition was selected. Electrocoagulation was performed for 10 minutes at an electric current density of 0.005 A/cm^2. Before treatment, an alkaline additive was added to the wastewater, which allowed to vary the pH from 4.0 to 8.7. The results obtained are presented in Table 1.

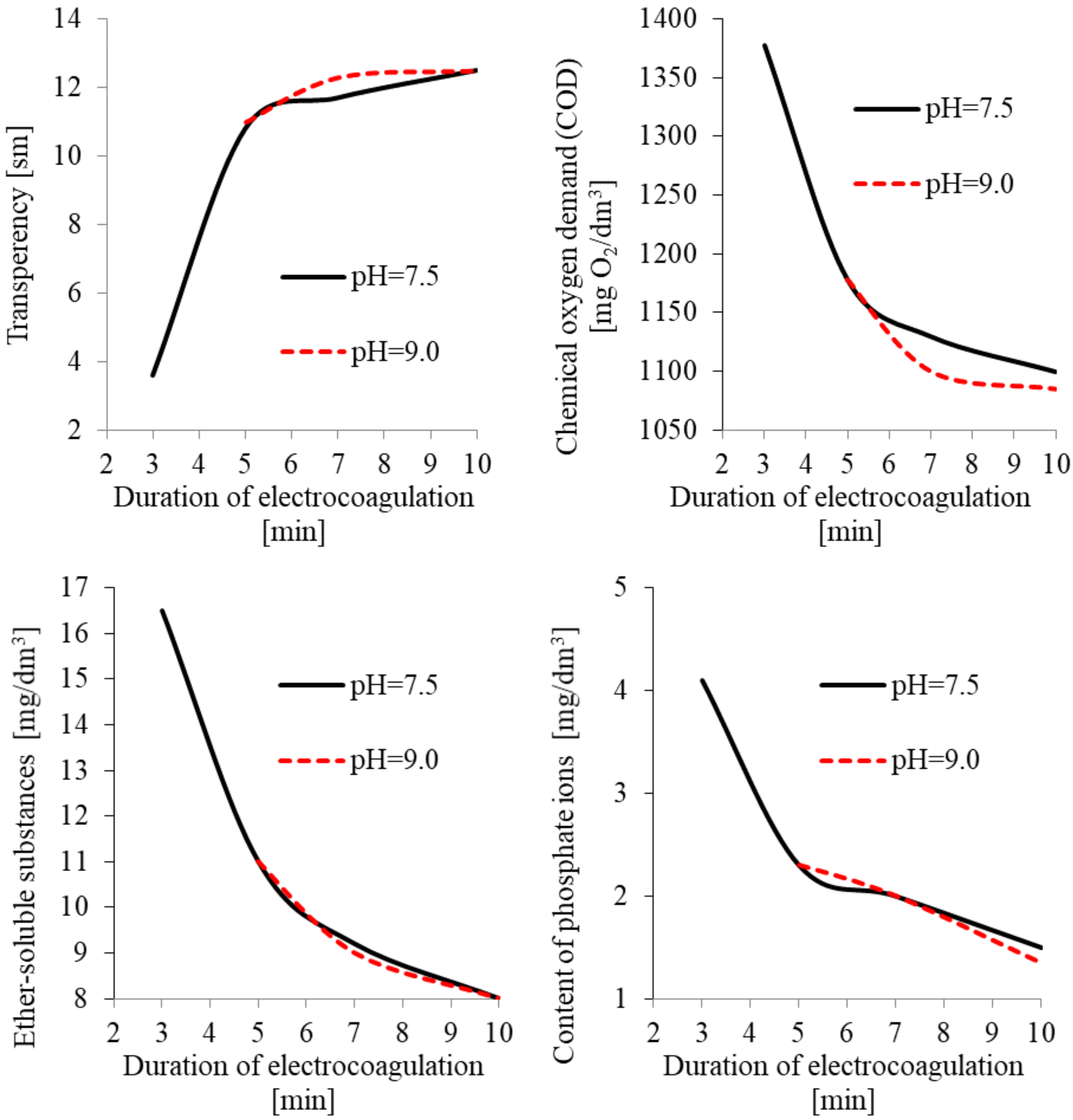
Table 1. The effect of pH on the patterns of coagulant formation and wastewater treatment efficiency

pH		COD, $[mgO/dm^3]$	ESS, $[mg/dm^3]$	Purification effect, [%]	
to electrocoagulation	after electrocoagulation			from COD	from ESS
4.0	-	12000	1260	-	-
4.0	5.0	1200	22	90.0	98.3
4.9	5.6	1200	9	90.0	99.3
5.8	6.2	1200	7	90.0	99.4
6.7	7.2	1100	7	90.9	99.4
7.6	7.2	1100	5	90.9	99.6
8.7	7.2	1080	2	91.0	99.9

As can be seen from the presented results, after electrocoagulation of wastewater without the addition of alkaline additives, the degree of purification by COD and ESS is 90 and 98.3%, respectively. Addition before treatment of an alkaline additive to the pH of the source water 4.9-5.8 does not affect the degree of purification by COD and slightly increases (approximately 1%) the degree of purification by ESS. The pH of the water after electrocoagulation increases. Therefore, it can be stated that electrochemical processes (1-3) occur in electrocoagulation in acidic and weakly acidic (pH ≈ 4.0-5.8) medium. The process of oxidation of water at the cathode (2) with the formation of OH^- ions predominates, which leads to a slight increase in the pH at the end of electrocoagulation. It is obvious that in such conditions the formation of aluminum complexes does not occur, which would inevitably lead to a decrease in pH. Therefore, it can be concluded that the electrocoagulation of acidic and weakly acidic wastewater (4<pH<6) mainly produces particles of molecular structure $Al(OH)_3$, which perform the main coagulating action and provide a certain degree of purification. At the same time the adsorption mechanism of removal of pollutants is realized to a greater extent.

If an alkaline additive is added before electrocoagulation to form a neutral and slightly alkaline medium, the following is observed after treatment. The degree of wastewater treatment is slightly higher, both for COD (by 1%) and for ESS (by 1.6%). The pH of the water after treatment remains neutral and does not depend on the amount of added alkaline additive. Obviously, this is due to additional acidification of the solution due to hydrolysis of monomeric $AlOH^{2+}$, $Al(OH)_2^+$ and polymeric $Al_2(OH)_2^{4+}$, $Al_2(OH)_5^+$, $Al_6(OH)_{15}^{3+}$, $Al_{13}(OH)_{34}^{5+}$ aluminum complexes formed in excess of OH^- ions. Electrochemical processes take place in water during neutral and weakly alkaline electrocoagulation (1,2,4). But the process of coagulant formation in the form of $Al(OH)_3$ (4) obviously does not occur. Therefore, in the electrocoagulation of neutral and weakly alkaline wastewater (9>pH>6) as coagulating substances are monomeric and polymeric aluminum complexes, which are charged particles. This provides a higher degree of wastewater treatment. At the same time the mixed mechanism of removal of pollutants is realized: along with adsorption electrostatic coagulating action is possible.

The results of the experiments suggested that the addition of alkaline additives may be more effective after the process of electrocoagulation of wastewater. To test this hypothesis, studies on electrocoagulation of wastewater with different process times – 3, 5, 7 and 10 minutes. The addition of alkaline additive to pH=7.5 and pH=9.0 was carried out after the electrocoagulation process. The treated water with the added alkaline additive was mixed. After filtration, the filtrate was determined for transparency, COD, ESS, the amount of phosphate ions and the amount of ammonium nitrogen ions. The results obtained are presented in Fig. 1 and in Table 2.



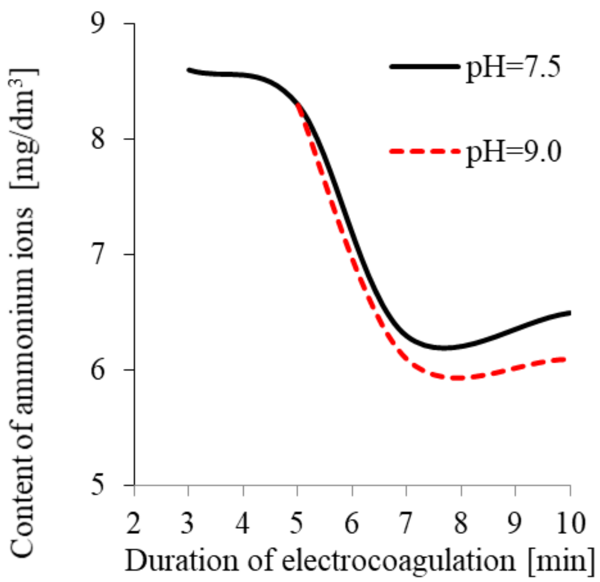


Fig. 1. Regularities of pH and electrocoagulation term influence on chemical composition of wastewater

Table 2. The effect of pH and electrocoagulation time on the degree of wastewater treatment

Duration of electrocoagulation [min]	pH	Purification effect [%]				
		for transparency	for COD	for ESS	for phosphate ions	for ammonium ions
3	7.5	83.2	73.1	97.5	97.2	14.3
5	7.5	94.4	77.1	98.3	98.4	17.5
7	7.5	94.9	78.0	98.6	98.6	37.7
10	7.5	95.2	78.6	98.8	99.0	35.0
5	9.0	94.5	77.1	98.3	98.4	17.5
7	9.0	95.1	78.6	98.6	98.6	39.0
10	9.0	95.2	78.8	98.8	99.1	39.0

Based on the results of the experiment, the following conclusions can be drawn. Regularities of the effect of pH and electrocoagulation time on the chemical composition of wastewater can be divided into two periods. The first period is limited to the period of electrocoagulation from 3 to 5 minutes. During this time, the degree of wastewater treatment from any contaminants does not depend on pH. The second period is limited to the period of electrocoagulation from 5 to 10 minutes. In this case, the pH value affects the degree of purification: with increasing pH, the degree of purification of wastewater from contaminants increases. Therefore, as can be seen from the presented data, the addition of alkaline additives after electrocoagulation is more efficient and will reduce the processing time. The degree of wastewater treatment will remain quite high (98-99%). This will save electricity and have a positive impact on the environmental and economic assessment of technology. Also from the obtained results it can be concluded that the pH value does not significantly affect the patterns of coagulant formation, the mechanism of coagulating action and the degree of wastewater treatment.

Conclusions

Researches of chemical-technological parameters of electrochemical production of coagulants on the basis of aluminum for electrocoagulation treatment of sewage of dairy processing enterprises are carried out. It is established that the efficiency of electrochemical formation and chemical nature of coagulants (metal hydroxides, complex ions) for electrocoagulation treatment of dairy waste directly depends on the process conditions: wastewater pH, the presence of various pollutants, strength or density of electric current, duration of electrocoagulation. The influence of pH and terms of the electrocoagulation process was studied in two cases of the technological process: when adding an alkaline additive before and after electrocoagulation treatment. In the case of the first case, the following conclusions can be drawn. Electrocoagulation of acidic and weakly acidic wastewater ($4<pH<6$) mainly produces particles of molecular structure $Al(OH)_3$, which perform the main coagulating action and provide a certain degree of purification. At the same time the adsorption mechanism of removal of pollutants is realized to a greater extent. In electrocoagulation of neutral and weakly alkaline wastewater ($9>pH>6$) as coagulating substances are monomeric and polymeric aluminum complexes, which are charged particles. This provides a higher degree of wastewater treatment. At the same time the mixed mechanism of removal of pollutants is realized: along with adsorption electrostatic coagulating action is possible. It was found that the addition of alkaline additives after electrocoagulation is more effective and will reduce the processing time. The degree of wastewater treatment remains quite high (98-99%). This will save electricity and have a positive impact on the environmental and economic assessment of technology.

References

[1] Ye. O. Makarov, Ekolohichna nebezpeka vysokokontsentrovanykh stichnykh vod molokopererobnykh pidpryiemstv. Stalyi rozvytok – stan ta perspektyvy: Materialy II Mizhnarodnoho sympoziumu SDEV’2020, Lviv, (2020) 235–236.

[2] V. A. Andronov, Yu. M. Danchenko, Ye. O. Makarov, T.M. Obizhenko, Research of the regularities of forming and chemical composition of sewage water of a dairy processing company, Technogenic and ecological safety, 7 (1/2020) 13–21.

[3] G. V. Sakash, A. F. Kolova, T. Ya. Pazenko, Ochistka stochnykh vod po pererabotke moloka, Vestnik KrasGAU, 8 (2016) 97–103.

[4] T. A. Shevchenko, A. A. Shevchenko, Eksperimentalnoie issledovaniie intensifikatsii protsessa napornoi flotatsii pri ochistke stochnykh vod molokopererabatyvaiushchego predpriiatiia, Vostocho-Yevropeiskii zhurnal peredovykh tekhnologii, 1/6 (79) (2015) 4–12.

[5] M. Konevych, V. Hud, Osoblyvosti stichnykh vod molokozavodiv. Materialy XV naukovoy konferentsii TNTU imeni Ivana Puliuia, Ternopil, (2011) 309.

[6] T. Yu. Gumerov, Kompleksoobrazovaniie v protsessakh koaguliatsii I flokuliatsii belkovo-lipidnykh kolloidnykh system, Dissertatsiya na soiskaniie uchenoi stepeni kamdidata khimicheskikh nauk, Kazan, (2006) 173.

[7] Vladimir Andronov, Yevhen Makarov, Yuliya Danchenko, Tatyana Obizhenko, Colloid-chemical regularities of reagent wastewater treatment of dairies, Materials Science Forum, 1038 (2021) 235-241.

[8] S. B. Zuieva, I. N. Matiushchenko, E. O. Nozdrina, Osobennosti koaguliatsionnoy ochistki stochnykh vod molochnoy promyshlennosti s ispolzovaniiem filtratsionnogo osadka sveklosakharnogo proizvodstva, Voda: khimiia i ekologiia, 6 (2012) 76–79.

[9] Yu. A. Feofanov, N. L. Litmanova, Ob effektivnosti koaguliatsionnoi ochistki stochnykh vod predpriiatiy molochnoy promyshlennosti, Izvestiia Vuzov, Khimiia I khimicheskaia tekhnologiia, 48, 3 (2005) 113–115.

[10] Yu. A. Feofanov, N. L. Litmanova, Mekhanizm koaguliatsioonoy ochistki stochnykh vod oksokhloridom aliuminiia, Zhurnal prikladnoy khimii, 74, 8 (2001) 337–339.

[11] Gerson de Freitas Silva Valente, Regina Celia Santos Mendonca, Jose Antonio Marques Pereira, The efficiency of electrocoagulation using aluminum electrodes in treating wastewater from a dairy industry, Ciencia Rural, Santa Maria, 45, 9, (2015) 1713–1719.

[12] B. Chezeau, L. Boudriche, C. Vial and A. Boudjemaa, Treatment of dairy wastewater by electrocoagulation process: Advantages of combined iron/aluminum electrodes (published online 15.07.2019), Separation Science and Technology, 15 (2019).

[13] A. Aitbara, M. Cherifi, S. Hazourli and J.-P. Leclerc, Continuous treatment of industrial dairy effluent by electrocoagulation using aluminum electrodes, Desalination and Water Treatment, 57, 8 (2016) 3395–3404.

[14] F. Benaissa, H. Kermet-Said and N. Moulai-Mostera, Optimization and kinetic modeling of electrocoagulation treatment of dairy wastewater, Desalination and Water Treatment, 57, 13 (2016) 5988–5994.

[15] G. Varank, M. E. Sabuncu, Application of central composite design approach for dairy wastewater treatment by electrocoagulation using iron and aluminum electrodes: modeling and optimization, Desalination and Water Treatment, 56, 1 (2015) 33–54.

[16] Shariff Ibrahim, Nur Syuhaidah Mohd Aris, Borhannuddin Ariffin, Yahaya Hawari and Megat Ahmad Kamal Megat Hanafiah, Application of electrocoagulation process for decolourisation of palm oil mill effluent (POME), Nature Environment and Pollution Technology, 17, 4 (2018) 1267-1271.

[17] A. Izadi, M. Hosseini, G. N. Darzi, G. N. Bidhendi, F. P. Shariati, Treatment of paper-recycling wastewater by electrocoagulation using aluminum and iron electrodes, Journal of Environmental Heals Science and Engineering, 16 (2018) 257-264.

[18] S. Yilmaz, E. Estra Gerek, Y. Yavuz and A. S. Koparal, Treatment of vinegar industry wastewater of electrocoagulation with monopolar aluminum and iron electrodes and toxicity evaluation, Water Science & Technology, in press (2019) 1-11.

[19] Y. A. Quaissa, M. Chabani, A. Amrane and A. Bensmaili, Removal of tetracycline by electrocoagulation: Kinetic and isotherm modeling through adsorption, Journal of Environmental Chemical Engineering, 2, 1 (2014) 177-184.

[20] M. Murugananthan, G. Bhaskar Raju, S. Prabhakar, Separation of pollutants from tannery effluents by electro flotation, Separation and Purification Technology, 40, 1 (2004) 69-75.

[21] I. Zongo, A. H. Maiga, J. Wethe, G. Valentin, J. P. Leclerc, G. Paternotte, F. Lapicque, Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: compared variations of COD levels, turbidity and absorbance, Journal of Hazardous Materials, 169, 1-3 (2009) 70-76.

[22] M. Changmai, M. Pasawan & M. K. Purkait, Separation and purification technology treatment of oily wastewater from drilling site using electrocoagulation followed by microfiltration, Separation and Purification Technology, 210 (2019) 463-472.

[23] Yu. Yu. Lurie, Analiticheskaia khimiia promyshlennykh stochnykh vod, (1984) 448.

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Improving Occupational Safety and Health in the Processing of Metallurgical Waste and Features of their Microstructure Transformation

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Abstract. The physicochemical properties of the alloy obtained by reductive melting with the use of waste from the production of high-alloy steels and alloys have been studied. This is necessary to determine the technological aspects that reduce the loss of alloying components during the production and use of the alloying alloy. The research results indicate that the alloy treasure is represented by iron phases with the content of alloying elements as substitution atoms. The proportion of residual carbon, which was part of the carbide component and the residual unproduced reducing agent, provided the necessary reducibility during the use of the alloy. The microstructure of the alloying alloy was characterized by the presence of phase formations that differed in shape, size and chemical composition. The content of Ni in the studied areas of different phases varied in the range of 1.28–32.62 % wt., Cr-0.33–46.22 % wt., W-0.00–20.43 % wt., Mo – 0 .00–10.78 % wt. Mo, W, Nb were more concentrated in individual particles, which probably had a carbide nature. The research identified new technological aspects of processing high-alloy man-made waste to obtain the resource-saving alloying alloy with the possibility of replacing part of the standard ferroalloys in steelmaking. Indicators of the obtained alloy allow to smelt grades of alloy steels when replacing part of standard ferroalloys. Production and use of alloying alloy eliminates the need for storage of fine oxide metallurgical waste on the territory of enterprises. This allows to improve the sanitary conditions of workers to increase the level of safety of residents of the surrounding areas without additional costs for the maintenance of waste storage sites.

Introduction

The current state of metallurgical production is characterized by the formation of the significant amount of waste that accumulates in the dumps, occupying the area of possible treated land and polluting the surrounding area [1]. Especially dangerous for the environment is the presence in the waste of heavy metals, which include Cr and Ni, which contaminate soils [2] and groundwater [3]. Cr and Ni according to the degree of danger of impact on living organisms belong to the 2nd class of danger (moderately dangerous) [4]. The maximum permissible concentrations in Cr and Ni soils in the EU country such as Bulgaria in residential areas are 200 and 100 mg/kg, respectively. In industrial areas – 300 and 250 mg/kg, respectively [5]. In Germany, the situation is somewhat different. In residential areas, the maximum allowable concentrations of Cr and Ni are 400 and 140 mg/kg, and in industrial facilities – 1000 and 900 mg/kg, respectively [4]. Once in the human body, Cr and Ni cause poisoning. The toxicity of Cr depends on its valence. Trivalent Cr has a relatively low toxic effect [6]. But hexavalent Cr has an acute toxic effect and is a carcinogen and mutagen

[7]. The toxic carcinogenic effect of Ni and Cr was also noted by the authors in [8]. At the same time, there was the effect of Ni and Cr on the human body with the emergence of diseases of the cardiovascular and nervous systems. From the above it follows that the disposal of chromium-nickel-containing wastes of metallurgical production can prevent pollution of land and water resources with heavy toxic elements. This prevents people who come into contact with the polluted environment from diseases of the cardiovascular, nervous systems and cancer.

Recycling and return to the production of man-made waste is one of the ways to obtain alloying materials of refractory elements, the prices of which tend to increase [9]. One of the ways to save resources is to obtain alloying materials containing molybdenum, tungsten, chromium, nickel by processing and returning to the production of alloyed man-made waste. A significant proportion are oxide and fine waste – grinding dust, scale. Effective processing of such waste is complicated. This causes problems in ensuring the manufacturability of production and reasonable cost of production. The specific feature of waste is the presence of alloying elements in the form of oxide and complex compounds. This necessitates taking into account the complex nature of the physical-chemical interaction of the elements in the development of technological conditions of processing.

Thus, the problem of improving the level of occupational safety and health in the processing of metallurgical waste with reducing the loss of alloying elements is relevant. This requires study of the peculiarities of physicochemical transformations in the reductive melting of oxide alloyed metallurgical wastes.

Analysis of Publications

As a method of processing oxide man-made raw materials in practice has positive results of reduction with carbon [10], as well as a complex of C and Si [11], with the production of fused products. The use of reductive smelting is possible in the processing of scale and other fine man-made waste contaminated with mineral oils and emulsions that require refining from harmful impurities.

Iron scale consists of Fe_3O_4, Fe_2O_3 and FeO, which was presented in [12], but in [13] WO_2 and $W_2C{\cdot}Mo_2C$ were also found in high-speed steel scale. The reason for this may be the increased level of alloying. The authors of [12] studied the reduction with carbon of iron scale in the range of 750–1050 °C with the detection of Fe_3C and C in the obtained products along with the iron phase. Residual iron oxides showed up only after heat treatment at 750 °C. Similar results with the detection of Fe_3C are presented in [14] in the reductive melting of alloyed oxide wastes with the content of Mo and Cr. In contrast, in [15] the additional presence of W probably had an impact on the nature of carbide formations, which was reflected in the features of the microstructure. Some particles, probably carbide, with high levels of carbon, tungsten and other elements were found. A similar trend was observed in [16]. Among the shortcomings is the lack of study on the physicochemical properties of reduction products involving refractory elements W and Nb. The unsolved parts of the problem are to determine the most favorable conditions for the recovery of doped man-made raw materials in the Fe-Ni-Cr-Mo-W-Nb-O-C system.

In [17] it was shown that the reduction of oxides in Mo-O-C system occurs with the transition of molybdenum trioxide to dioxide and free molybdenum with the formation of carbides. The reduction process in W-O-C system, which was studied in [18], was also characterized by the formation of intermediates $WO_{2.72}$ and WO_2. Tungsten dioxide was subsequently converted into metal tungsten and carbide component. Similar results are also given in [19]. The disadvantage is that the form of the presence of molybdenum- and tungsten-containing compounds in the oxide waste of high-alloy steels can be more complex and differ from individual pure oxides.

Reduction of $FeO{\cdot}Cr_2O_3$ oxides at different C:Fe atomic ratios and temperatures from 1373 K to 1523 K was investigated in [20]. It was determined that with increasing the atomic ratio of C:Fe from 0.8 to 1.4, the degree of extraction (%) of chromium increased from 9.6 to 74.3, respectively. Increasing the temperature to 1523 K led to the increase in the formation of carbides. According to the results of [21], some carbon residue is inevitably present in the products of carbon-thermal reduction. In this case, the residual carbon may be present in the form of carbide compounds. At

C:Fe atomic ratios below 0.8, the significant decrease in the degree of chromium extraction and decrease in carbide formation was observed. The formed chromium carbides dissolved in the iron phase [20]. In [22], the study of reductive reactions involving oxides and carbon in Fe-Ni-O system at temperatures up to 1373 K was performed. With increasing of the processing temperature, the reduction products were manifested in the following sequence: Fe_3O_4+NiO→Fe_3O_4+Ni→FeO+Fe_xNi_y→Fe_xNi_y+Fe(Fe_nC_m). That is, there was the relatively greater tendency to reduce Nickel oxide than iron oxides. The formation of nickel and iron metals was observed at separate stages. The possibility of the presence of iron carbides and iron-nickel-containing phase Fe_xNi_y, which can also occur during the recovery of oxide alloyed waste. The disadvantage is the lack of data on the reduction of complex oxide compounds, which may be part of man-made raw materials. This can lead to probable differences in the course of the reduction reactions. Unresolved parts of the problem are to expand understanding of the nature of the presence of elements in the recovery products with the integrated use of scanning electron microscopy and X-ray microanalysis.

Therefore, it is expedient to study the features of the microstructure of alloying raw materials obtained by reductive smelting on the basis of the mixture of man-made waste steels and alloys alloyed with refractory elements. This will determine the nature of the presence of elements in the material. However, the use of X-ray microanalysis of individual inclusions and phases will expand the understanding of the distribution of alloying elements in the resulting alloy.

Object and Problem Statement

The goal of the work was to identify the features of structural transformations in the processing of high-alloy oxide dispersed wastes of metallurgical production using reductive melting and obtaining the alloy containing Ni, Cr, W, Mo, Nb, as well as to identify harmful factors associated with the formation and storage of man-made waste, and ways to eliminate them. This is necessary to determine the parameters that reduce the loss of alloying elements in the processing of oxide alloying raw materials and the use of the obtained alloying additives, as well as improving occupational safety and health in the processing of metallurgical waste.

To achieve this goal, the following objectives were set:

– to determine the features of the microstructure of the alloying alloy on the basis of man-made waste with the study of the chemical composition of individual phases and inclusions of resource-saving alloying alloy in relation to the nature of the presence of elements.

– identify harmful factors associated with the formation and storage of man-made waste, and ways to eliminate them.

Material and Methods of Study

The raw material is the mixture of scale of chrome-nickel-containing steels type 18–10 and chips of grinding heat-resistant alloys based on nickel EI893 and EP709, formed in areas of metallurgical production. The addition of metal chips provided intensification of heat transfer in the initial stages of heating the charge and further increase of the alloy. Reduction agent - carbon, in the form of ultrafine dust from carbon production (carbon content – 98 % wt.), the regulation of the amount of which provided the ratio of O:C in the charge of 1.33. Samples for research were smelted in the indirect heating furnace with coal lining in alundum crucibles. Smelting temperature – 1873–1913 K. After smelting, alundum crucibles together with the alloy were removed from the furnace and cooled at ambient temperature.

Images of the microstructure and chemical composition of individual areas of the sample surface were obtained on the scanning electron microscope "JSM-IT300" from JEOL (Japan), with X-ray microanalysis system "X-MAX80" from Oxford Instruments (UK). The study of the microstructure of the samples was performed at the accelerating voltage of 10–25 kV and electron probe current of 52–96 µA. The working distance to the studied surface was 10.5–11.7 mm.

Main Material of Study

Determining the Features of the Microstructure of the Alloying Alloy. It was found that the microstructure of the alloying alloy is heterogeneous and characterized by the presence of several variations of phase formations with different indicators of element content (Fig. 1–3, Table 1). The content of Ni in the studied areas of different phases varied in the range of 1.28–32.62 % wt., Cr – 0.33–46.22 % wt., W – 0.00–20.43 % wt., Mo – 0.00–10.78 % wt. The carbon content in the predominant number of measurements was in the range of 0.46 to 2.45 % wt. Mo, W, Nb were more concentrated in individual particles, which probably had a carbide nature. The Nb content in the studied areas reached a value of 1.92 % wt. Individual particles with relatively high carbon content up to 96.14 % wt. (Fig. 1, points 7, 8) may be areas of residual carbon reductant, which will be produced during doping and further increase the reducibility of the alloy when dissolving and assimilating refractory elements in steel.

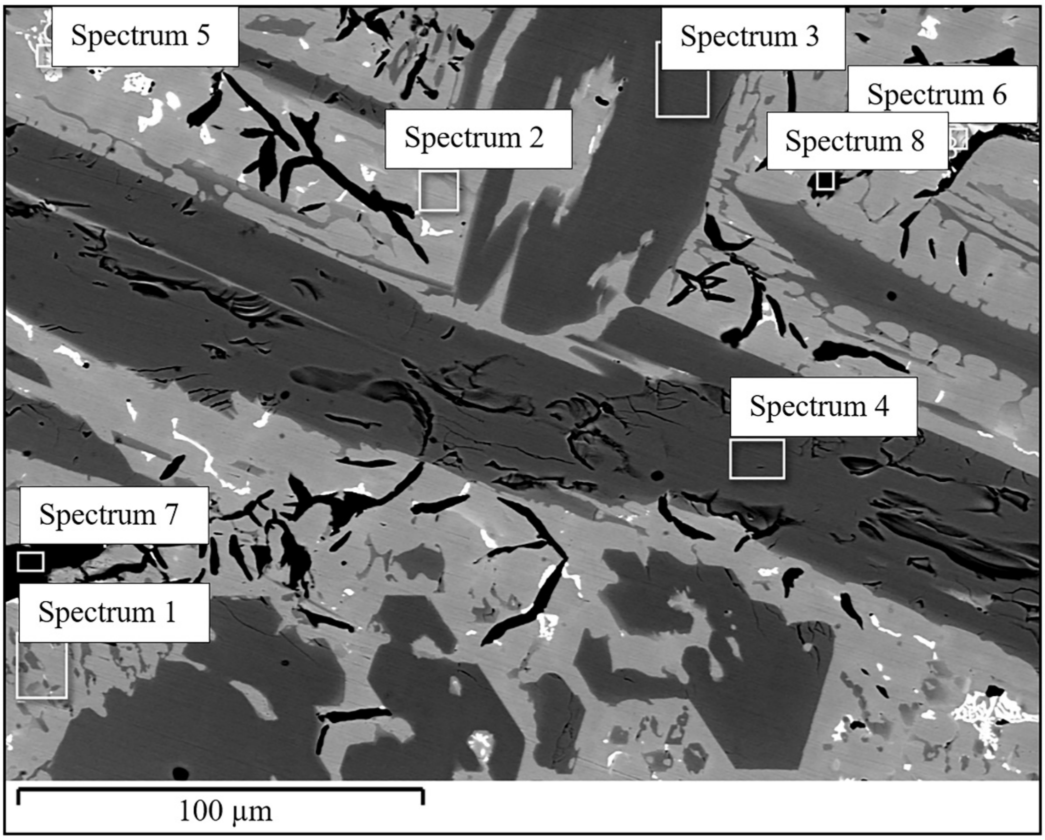

Fig. 1. Investigation of the microstructure of the alloying alloy at an O:C ratio in the charge of 1.33 with the increase of ×500: 1–8 – areas of X-ray microanalysis of samples

Table 1. The results of X-ray microanalysis of the alloying alloy, respectively, Fig. 1

No. Sr.	Content of elements, [% wt.]									
	C	Al	Cr	Mn	Fe	Ni	Zr	Nb	Mo	W	Total
1	0.53	0.1	11.73	0.25	50.84	32.62	0.00	0.00	1.44	2.49	100.00
2	0.46	0.12	11.65	0.23	51.04	30.33	0.00	0.00	1.91	4.26	100.00
3	2.45	0.05	46.17	0.00	42.18	5.55	0.00	0.00	1.38	2.22	100.00
4	2.29	0.07	46.22	0.00	42.11	5.53	0.00	0.00	1.30	2.48	100.00
5	1.07	0.15	6.44	0.00	37.91	20.34	0.96	1.92	10.78	20.43	100.00
6	2.14	0.07	6.69	0.00	41.05	19.45	1.17	0.74	9.57	19.12	100.00
7	96.14	0.00	0.33	0.00	2.25	1.28	0.00	0.00	0.00	0.00	100.00
8	84.20	0.00	2.62	0.00	8.08	5.10	0.00	0.00	0.00	0.00	100.00

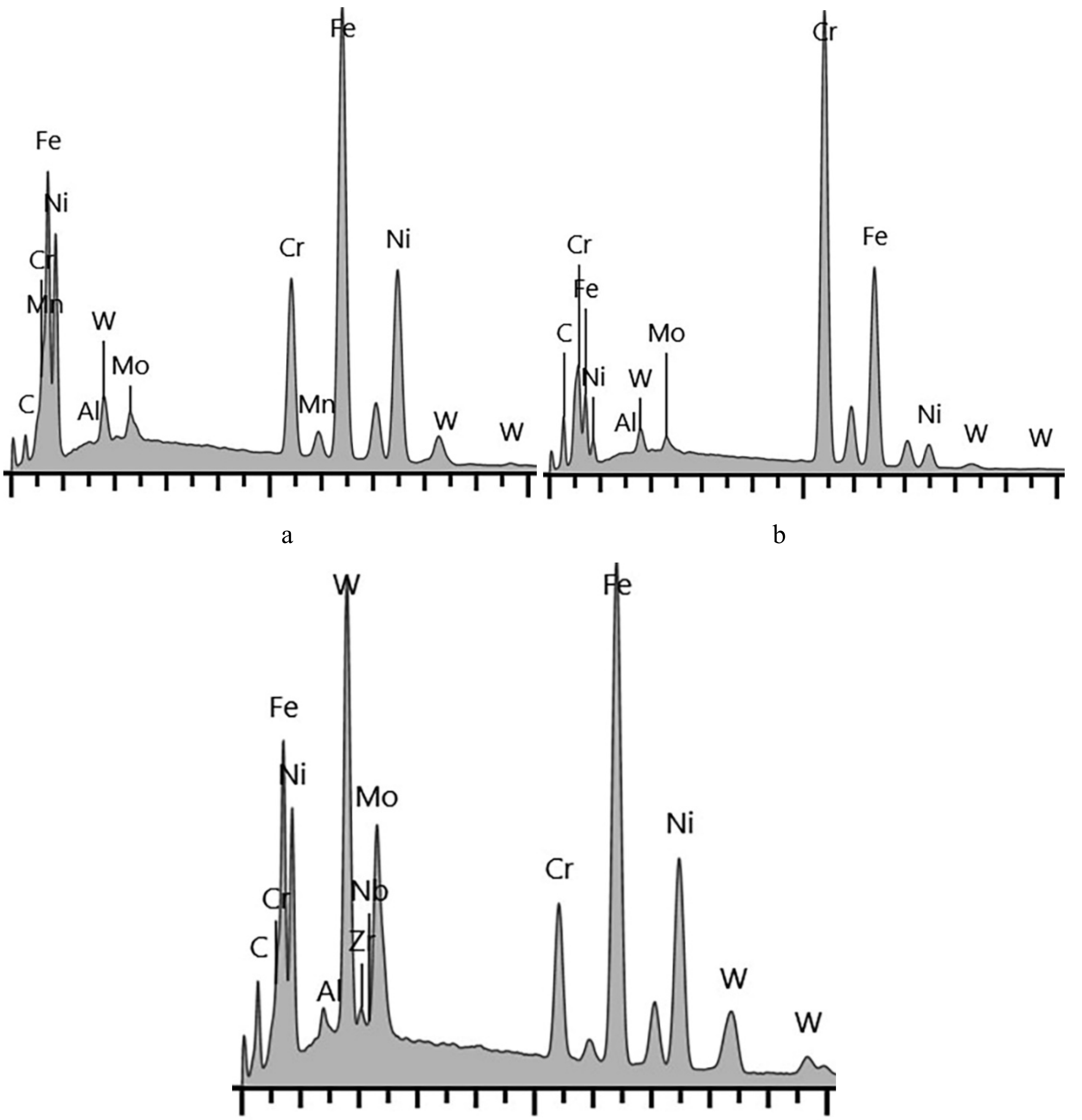

Fig. 2. Spectrograms of some of the areas of X-ray microanalysis of the alloying alloy, respectively, Fig. 1: *a* – 2, *b* – 3, *c* – 6

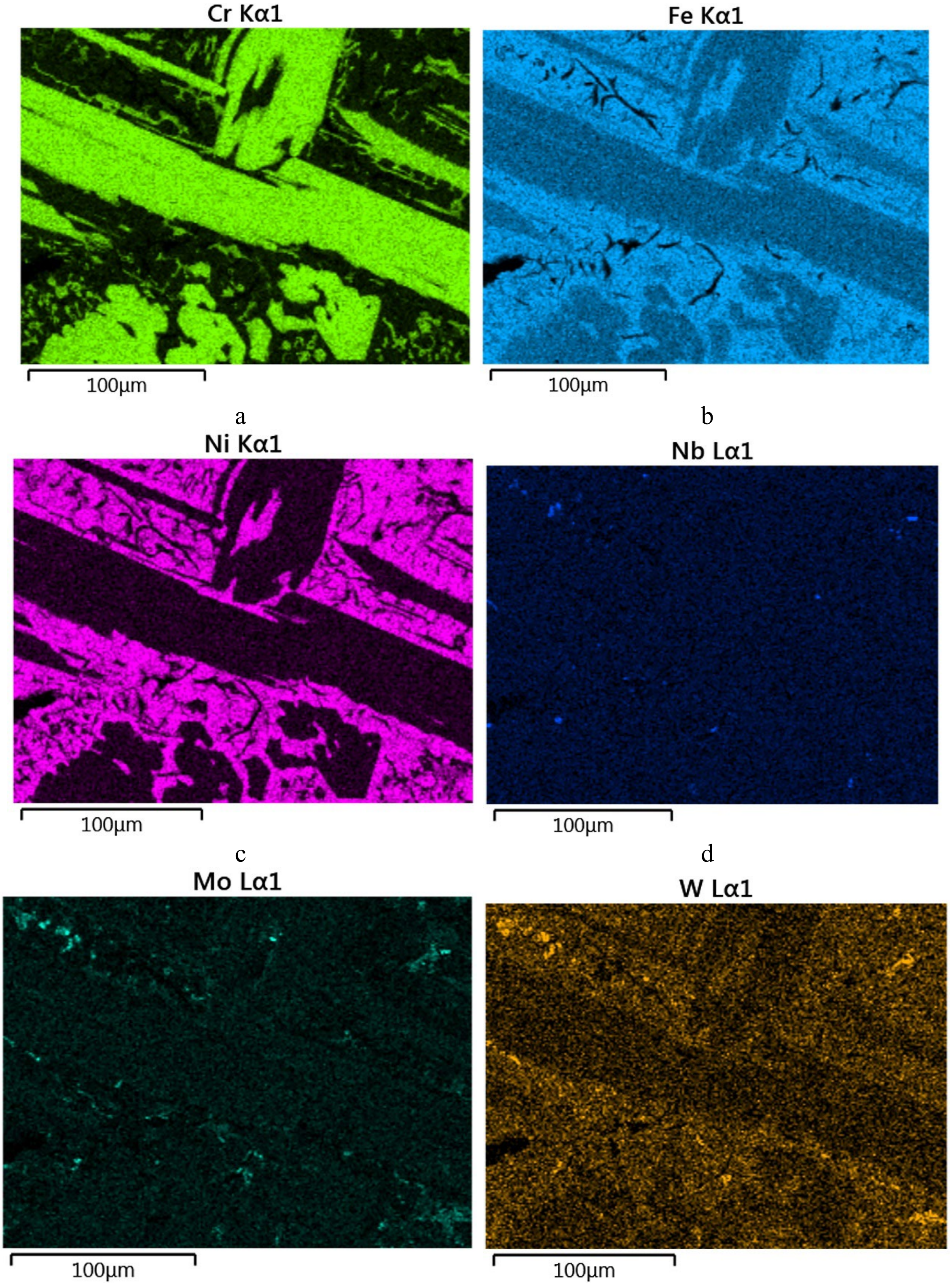

Fig. 3. The distribution of the main elements in the characteristic X-rays, respectively, Fig. 1 (magnification ×500). The higher the content of the element corresponds to the more intense brightness: *a* – C, *b* – V, *c* – Cr, *d* – Fe, *d* – Co, *e* – Mo, f – W

The study of the distribution of elements (Fig. 3) indicates the coincidence of the zones of concentration of Fe and Ni. The presence of Al, Mn, Zr had the relatively low and fragmentary manifestation at the level of concomitant impurities.

The study of the microstructure in combination with X-ray microanalysis of the obtained alloy (Fig. 1) indicates that, probably, the alloying elements were in solid solution in the iron lattice. Some of the alloying elements could be in the form of carbide iron-containing compounds. This is consistent with the results of [11], where on the diffraction pattern of the reduced doped product only iron-containing compounds had a clear manifestation. There is also compliance with the results of [16] on the parallel course of reduction and carbide formation and the impossibility in practice to obtain the completely carbon-free product. In this case, the absence of the clear manifestation of phases of refractory elements in these studies is apparently associated with the concentration of most of the alloying elements as substitution atoms in iron carbides and the solid solution in the iron lattice. Phases with high content of Ni and Fe (points 1, 2) can be the solid solution of Fe_xNi_y . This is in good agreement with the results of [10, 14], which confirmed the relatively high efficiency of reduction of the iron-nickel oxide component with carbon. However, in [22] with the course of reduction processes together with Fe_xNi_y there was the iron-containing carbide component of Fe (Fe_nC_m). It is seen that some phases were characterized by high content of Cr and Fe (Table 1, points 3, 4). Such phases, apparently, may consist of Fe_3C, where Fe atoms are partially replaced by Cr atoms. This is consistent with the results of [20], which indicates the formation of chromium-containing carbides in parallel with the reduction. However, in [20] the reduction is accompanied by the formation of carbides Cr_3C_2, $Cr_{23}C_6$, Cr_7C_3. The absence of manifestation of individual chromium-containing phases in these studies is explained by the fact that it is possible to dissolve some of the carbides in the solid solution of the iron phase at the contact of the two phases.

Some particles with high content of Mo, W, Nb and C (Fig. 1, points 5, 6) may be carbide phases. This is in good agreement with the results of works on the reduction mechanism of W [18, 19] and Mo [17] oxides. It was found that at the final stage of recovery there is the parallel formation of metal and carbide components. In this case, as a difference, in these studies, the expected particles of the carbide phase are characterized by the high content of the complex of alloying elements. This indicates the more complex nature of the joints of refractory elements.

Analysis of research results showed that at O:C ratio of 1.33 in the charge, the alloy composition is represented by iron phases containing alloying elements as substitution atoms. The performed research identified new technological aspects of processing high-alloy man-made waste to obtain the alloy with the relatively low residual carbon content. The obtained parameters of the resource-saving alloying material provide the possibility of replacing part of the standard ferroalloys in the melting of steels that have some restrictions on carbon content. The austenitic heat-resistant steels are promising from this point of view.

Limitations of the research results are the use of the obtained alloying alloy in relation to certain classes of steels, based on the complex content of elements. For example, in some heat-resistant steels, the complex of elements Ni, Cr, Mo, W determines the required quality properties of the product. And in tool high-speed steels, in contrast to Cr, Mo, W, the content of Ni is strictly limited to ten percent. Therefore, the problem may be to increase the allowable limits of the composition of the elements in the target product. Similar problems are not excluded for other grades of steel, where there are serious restrictions on the content of one or more elements of the alloying alloy. Therefore, in order to avoid problems of this nature and increase the cost of use of raw materials, the close ratios of the content of elements in the alloying alloy and the target product should be followed. That is, the indicators of the obtained alloy allow to smelt grades of alloy steels when replacing part of the standard ferroalloys. From this point of view, heat-resistant steels are promising.

The development of this research is possible in the direction of expanding the range of classes of steels, oxide waste which will be involved in the processing by the method of reductive smelting. The difficulty in trying to develop this study is the lack of the sufficient experimental database. The most promising are wastes with the high level of doping.

Identification of Harmful Factors Associated with the Formation and Storage of Man-made Waste, and Ways to Eliminate Them. The formation and storage of fine oxide waste is accompanied by a number of dangers for both employees of metallurgical enterprises and residents of the surrounding areas. When stored outdoors in landfills, the fine nature of the generated waste contributes to the spread by the wind. At the same time, it is possible for wind-raised microparticles to enter the respiratory organs and other mucous membranes of workers. This can lead to deteriorating health with the development of respiratory diseases. Elements such as nickel and chromium, however, have the carcinogenic effect on the human body. Therefore, in addition to the irritating effect of mucous membranes with dust particles, toxic effects of the elements present in the composition are also possible.

In addition, the storage of waste may be accompanied by contamination of adjacent soils and groundwater. Together with groundwater, harmful toxic elements from waste can get into drinking water sources, which can cause disease in the population of the surrounding areas.

One of the options to reduce the harmful effects of the generated oxide waste is to improve the equipment of storage sites by eliminating contact with soils and precipitation. These can be covered areas or warehouses. It is also possible to use barrels or other containers.

The above measures are temporary and require additional storage and maintenance costs. In this regard, the processing of oxide waste generated in-house production is fundamentally the qualitative solution to the existing problem. Therefore, obtaining the alloying alloy based on man-made waste provides not only the development of resource conservation, but also the improvement of sanitary working conditions and increase the level of safety of the inhabitants of the surrounding areas.

Conclusions

1. The composition of the alloy is represented by iron phases containing alloying elements as substitution atoms. The proportion of residual carbon, which was part of the carbide component and the residual unproduced reducing agent, provided the necessary reducibility during the use of the alloy. The microstructure of the alloying alloy was characterized by the presence of phase formations that differed in shape, size and chemical composition. The content of Ni in the studied areas of different phases varied in the range of 1.28–32.62 % wt., Cr – 0.33–46.22 % wt., W – 0.00–20.43 % wt., Mo – 0.00–10.78 % wt. Mo, W, Nb were more concentrated in individual particles, which probably had a carbide nature. The research identified new technological aspects of processing high-alloy man-made waste to obtain the resource-saving alloying alloy with the possibility of replacing part of the standard ferroalloys in steelmaking. Indicators of the obtained alloy allow to smelt grades of alloy steels when replacing part of standard ferroalloys. From this point of view, heat-resistant steels are promising.

2. Storage of the generated fine oxide waste may cause fine particles of waste to enter the air and have the harmful irritant effect on the respiratory tract and mucous membranes of workers, as well as have the toxic effect. However, the storage of waste may be accompanied by contamination of adjacent soils and groundwater. To avoid these dangers, it is possible to improve the equipment of storage sites by eliminating contact with soil and weather elements. These can be covered areas or warehouses. It is also possible to use barrels or other containers. Production and use of alloying alloy eliminates the need for storage of fine oxide metallurgical waste on the territory of enterprises. This allows to improve the sanitary conditions of workers to increase the level of safety of residents of the surrounding areas without additional costs for the maintenance of waste storage sites.

References

[1] R.Q. Puchol, E.R. Sosa, L.O. Gonzalez, Y.P. Castaneda, L.Y. Sierra, New conception of the reutilization of solid waste from Cuban nickeliferous hydrometallurgical industry, Centro Azucar. 43, 4 (2016) 1–15.

[2] I. Pincovschi, N. Neacsu, C. Modrogan, The Adsorbtion of Lead, Copper, Chrome and Nickel Ions from Waste Waters in Agricultural Argilaceous Soils, Revista de Chimie. 68, 4 (2017) 635–638.

[3] V. Madebwe, C. Madebwe, A. Munodawafa, F. Mugabe, Analysis of the Spatial and Temporal Variability of Toxic Heavy Metal Concentrations in Ground Water Resources in Upper Sanyati Catchment, Midlands Province, Zimbabwe, IIARD International Journal of Geography and Environmental Management. 3, 1 (2017) 23–37.

[4] I. Rubezhniak, Assessment of Standards of Heavy Metals Contaminated Soils in Ukraine and the EU Countries, Scientific Bulletin of the National University of Life and Environmental Sciences of Ukraine, Series: Biology, Biotechnology, Ecology. 234 (2016) 228–238.

[5] D.A. Eastmond, J.T. MacGregor, R.S. Slesinski, Trivalent Chromium: Assessing the Genotoxic Risk of an Essential Trace Element and Widely Used Human and Animal Nutritional Supplement, Critical Reviews in Toxicology. 38, 3 (2008) 173–190.

[6] N. Itankar, Y. Patil, Management of Hexavalent Chromium from Industrial Waste Using Low-cost Waste Biomass, Procedia – Social and Behavioral Sciences. 133, 5 (2014) 219–224.

[7] Y. Chervona, A. Arita, M. Costa, Carcinogenic metals and the epigenome: understanding the effect of nickel, arsenic, and chromium, Metallomics. 4, 7 (2012) 619–627

[8] I. Atanassov, New bulgarian soil pollution standards, Bulgarian Journal of Agricultural Science. 14 (2008) 68–75.

[9] M.L.C.M. Henckens, E.C. Van Ierland, P.P.J. Driessen, E. Worrell, Mineral resources: Geological scarcity, market price trends, and future generations, Resources Policy. 49 (2016) 102–111.

[10] V. Borysov, A. Lytvynov, N. Braginets, A. Petryshchev, S. Artemev, B. Tsymbal, A. Poliakov, V. Bratishko, V. Kuzmenko, O. Kholodiuk, Features of the phase and structural transformations in the processing of industrial waste from the production of high-alloyed steels, Eastern-European Journal of Enterprise Technologies. 3, 10(105) (2020) 48–54.

[11] A. Petryshchev, N. Braginec, V. Borysov, V. Bratishko, O. Torubara, B. Tsymbal, S. Borysova, S. Lupinovich, A. Poliakov, V. Kuzmenko, Study into the structural-phase transformations accompanying the resource-saving technology of metallurgical waste processing, Eastern-European Journal of Enterprise Technologies. 4, 12(100) (2019) 37–42.

[12] S. Mechachti, O. Benchiheub, S. Serrai, M. Shalabi, Preparation of iron Powders by Reduction of Rolling Mill Scale, International Journal of Scientific & Engineering Research. 4, 5 (2013) 1467–1472.

[13] S. M. Grigor'ev, A. S. Petrishchev, Assessing the Phase and Structural Features of the Scale on P6M5Ф3 and P12M3K5Ф2 Steel, Steel in Translation. 42, 3 (2012) 272–275.

[14] A. Petryshchev, D. Milko, V. Borysov, B. Tsymbal, I. Hevko, S. Borysova, A. Semenchuk, Studying the physical-chemical transformations at resource-saving reduction melting of chrome-nickel-containing metallurgical waste, Eastern-European Journal of Enterprise Technologies. 2, 12(98) (2019) 59–64.

[15] V. Volokh, E. Kim, T. Fesenko, A. Petryshchev, S. Artemev, B. Tsymbal, L. Makarenko, A. Hedzyk, V. Slabko, V. Khmelovskyi, Identifying the features of structural and phase transformations in processing the waste of metallurgical products doped with refractory elements, Eastern-European Journal of Enterprise Technologies. 5, 12(107) (2020) 32–38.

[16] A. Poliakov, A. Dzyuba, V. Volokh, A. Petryshchev, B. Tsymbal, M. Yamshinskij, I. Lukianenko, A. Andreev, T. Bilko, V. Rebenko, Identification of patterns in the structural and phase composition of the doping alloy derived from metallurgical waste processing, Eastern-European Journal of Enterprise Technologies. 2, 12(110) (2021) 38–43.

[17] H.Y. Zhu, Z.B. Li, H.S. Yang, L.G. Luo, Carbothermic Reduction of MoO3 for Direct Alloying Process, Journal of Iron and Steel Research, International. 20, 10 (2013) 51–56.

[18] G.P. Shveikin, N. A. Kedin, Products of carbothermal reduction of tungsten oxides in argon flow, Russian Journal of Inorganic Chemistry. 59, 3 (2014) 153–158.

[19] V. Ryndiaiev, O. Kholodiuk, V. Khmelovskyi, A. Petryshchev, A. Yushchenko, G. Fesenko, Y. Chaplyhin, V. Strelnikov, A. Andreev, V. Matukhno, Establishing patterns of the structural-phase transformations during the reduction of tungstencontaining ore concentrate with carbon, Eastern-European Journal of Enterprise Technologies. 1, 12(109) (2021) 16–21.

[20] L. Zhao, L. Wang, D. Chen, H. Zhao, Y. Liu, T. Qi, Behaviors of vanadium and chromium in coal-based direct reduction of high-chromium vanadium-bearing titanomagnetite concentrates followed by magnetic separation, Transactions of Nonferrous Metals Society of China. 25, 4 (2015) 1325–1333.

[21] I. V. Ryabchikov, B. F. Belov, V. G. Mizin, Reactions of metal oxides with carbon, Steel in Translation. 44, 5 (2014) 368–373.

[22] Y. Zhang, W. Wei, X. Yang, F. Wei, Reduction of Fe and Ni in Fe–Ni–O systems, Journal of Mining and Metallurgy, Section B: Metallurgy. 49, 1 (2013) 13–20.

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Study of Short-Term Effects on the Soil of Disposable Protective Face Masks Used in the COVID-19 Pandemic

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Abstract: The paper analyzes the impact of personal protective equipment used by the population as a result of the COVID-19 pandemic on the environment. The scale of the additional amount of waste generated as a result of the use of protective face masks, etc. is noted. The globality of the existing problem and its multiparametric impact on the components of the environment are indicated. The short-term effect of a number of disposable protective face masks on the condition of soil by chemical component has been studied. The dependence of leaching of heavy metals from masks on soil acidity was experimentally analyzed, the dynamics of mobile phosphorus and potassium in soil samples was studied. It is shown that the presence of masks in the soil leads to exceeding the standard for zinc content, while for copper content and manganese content exceeding the standard is not observed in the study period, for lead there are fluctuations in content beyond standard value. The need for long-term research on the impact of face masks on the environment, and in particular soils, was noted.

Introduction

The environment is constantly changing due to both natural and anthropogenic factors. Direct processes that constantly take place in man-made and natural environments can be assessed and taken into account in various models of their development. Whereas for emergencies of different levels and origins, the question of accurately determining the initial factors of their occurrence and development is quite difficult. In turn, this significantly complicates the assessment and minimization of such impacts on the environment and humans.

At the same time, it can be noted, for example, that in the case of fires, different solutions are offered that take into account the environmental component of fire extinguishers [1], their chemical composition [2] or, in general, their lack of use [3, 4]. It is also possible to use special measures to prevent the spread of fires [5], considering the features of firefighting [6, 7], preventive use of fire-resistant materials [8].

In the case of some other types of emergencies, the issue of their prevention or assessment may be even more complex, requiring additional determination of physical [9] or chemical [10, 11] environmental parameters, which may occur in earthquakes or industrial accidents. A complication is also the need to involve third-party equipment, in particular, electrical monitoring and surveillance systems in case of prevention of terrorist emergencies [12].

In turn, examples of emergencies that are very difficult to assess are emergencies with soil and water pollution due to the prevention of medical and biological emergencies.

Thus, the emergence of the COVID-19 pandemic, which is a medical and biological emergency, was almost impossible to take into account and, moreover, to accurately assess its impact on the world's population and the environment.

Today, it is one of the major challenges for humanity, causing significant casualties in different countries and affecting the modern world.

The COVID-19 pandemic has also led to additional requirements for public safety measures. Among the necessary elements of protection in many countries is the need for personal protective equipment (PPE) such as masks, respirators, gloves. These PPE can be both disposable and reusable, but in both cases there is a problem of their further disposal, which is particularly acute in the context of a global strategy to reduce waste [13].

Thus, a significant surge in demand for these products has led to the release into the environment of a large number of used PPE that clutters urban areas [14] and the natural environment [15].

Today, various countries have already noted the problem of accumulation of masks, gloves, etc. in the environment and the subsequent negative consequences of this. In particular, on the example of Bangladesh, the authors [16] predict the daily generation of 472 tons of plastic waste from disposable masks, bottles with disinfectant solution, gloves and more. Only the use of test for confirmation of COVID-19 is real-time PCR (RT-PCR) leads to the generation of 15.000 tons of waste worldwide [17]. Accordingly, under the condition of their mass accumulation, plastic and microplastics can be released into the environment directly [18], as well as chemical compounds of different composition [19].

In many studies, special attention is paid to protective face masks, which are widely used in different countries in the COVID-19 pandemic.

Thus, there is contamination of seawater with microplastics from surgical masks, which are recommended for use by the population in the COVID-19 pandemic [20]. The authors note secondary microplastic contamination from various types of PPE coastlines of the Persian Gulf [21], beaches of South America [22], Bangladesh [23], Ethiopia [24].

The release of tens of thousands of microfibers due to mechanical abrasion of surgical masks released into the environment due to the COVID-19 pandemic has been noted [25].

The authors [26] note the further negative impact of nanofibers used face masks on soil ecosystems, in particular, on representatives of the earthworm and springtail species.

Negative effects from unorganized storage and disposal of a significant number of protective face masks are noted in [27, 28]. The authors [29] point out that in the first year of the pandemic alone, 3.5 million metric tons of masks were formed, which significantly affects the management of solid waste in landfills and the emergence of additional amounts of microplastics in the environment. There are also prospects for the use of traditional and innovative technologies for the management of such waste.

As a way to solve the problem of reducing waste, it is proposed to use natural fibers and bio-renewable materials in the production of masks. Various options for disposal of these PPE are considered, in particular, pyrolysis, incineration, as well as economic levers for the management of this group of waste [30, 31]. It is also proposed to reuse them, for example for reinforcement in granular soil. [32] or to improve the mechanical characteristics of fat clay by adding as reinforced fiber [33].

At the same time, chemicals contained in anthropogenic products, under the influence of various external factors, can migrate into the environment [34]. PPE used in the COVID-19 pandemic is characterized by a certain chemical composition. The widespread use of this PPE, including protective masks of various compositions and origins, does not allow to state unequivocally the absence of chemical effects on the environment [35].

Thus, the authors [36] note that various organic (phthalates, organophosphorus and phenolic compounds, polymers, etc.) and inorganic (cadmium, antimony, copper) compounds are contained in protective equipment, including face masks. Moreover, the content of these substances is not regulated for face masks. Accordingly, as the authors note, the issue of quantitative and qualitative pollution of the environment with chemical compounds from face masks and their impact on biota requires further research.

Given the above, the current issue is to understand the chemical processes that occur when protective masks enter the environment with the subsequent adoption of the necessary management decisions in the field of environmental protection and in other areas.

The aim of the work is to study the effects of the chemical composition of protective face masks on the components of the environment, in particular, on the soil.

Materials and Methods

Reagents, materials and equipment.

The following reagents, materials and equipment were used in the experimental part:

– sodium hydroxide, sulfuric acid, hydrochloric acid, nitric acid, potassium chloride, ammonium molybdate, potassium sulfate, ascorbic acid, potassium dihydrogen phosphate, potassium oxide, standard samples of solutions 0.1 g/l Me (Cu, Zn, Mn, Pb) (Ukraine), distilled water. All reagents qualification "pure for analysis" and purer.

– laboratory balance AS 220.R2; SF-46 spectrophotometer; pH - meter pH - 150 MI (±0.02 pH accuracy); flame photometer; atomic adsorption spectrophotometer C 115 M1; laboratory glassware (flasks, beakers, pipettes, funnels), laboratory balanceTVE-0,21-0,001-a; sieve with holes of 1 mm; mortar and pestle.

All necessary solutions are prepared by diluting more concentrated solutions or by taking the necessary samples on appropriate laboratory balance and their subsequent dissolution.

The study used medical masks from Abipharm (Mask 1) and Maddins (Mask 2).

The study was performed by measuring parameters every 10 days. In total 4 measurements were made.

Sample preparation of soil for chemical analysis.

In a container with soil at a depth of 8–10 cm from the soil surface was laid 5 masks from the manufacturer. 150 ml of tap water, 0.1 M hydrochloric acid or 0.1 M NaOH were added to each container, respectively. A similar procedure was performed after each sampling from the contaners on the 5th, 15th, 25th day of the study.

A soil sample for research was taken at a depth of 8–10 cm from a container containing a certain set of test masks. Subsequently, this sample is dried by the dry-air method and homogenized to a grain size of 5 - 7 mm. The soil is a typical soil sample of the Kharkiv region (chernozem). For research using the quartering method, an average sample weighing 10–30 g is obtained.

Determination of pH of water soil extract.

30 g of soil are placed in a 250 ml beaker, distilled water is added in a ratio of 1:5 and stirred for 5 minutes. The suspension is filtered using a "white tape" filter, and the pH of the resulting water soil extract is measured.

The determination of mobile phosphorus and potassium is carried out according to the Kirsanov method, based on soil treatment with a 0.2 M HCl solution at a soil to solution ratio of 1:5 for mineral soils, followed by photocolorimetric determination of phosphorus and flame photometric determination of potassium.

Determination of mobile phosphorus in soil.

Preparation of reagent A. 6 g of ammonium molybdate are weighed on laboratory balance, transferred to a beaker and dissolved in 200 ml of distilled water. Weigh 0.155 g of potassium sulfate on laboratory balances and dissolve in a beaker in 100 ml of distilled water. Both solutions are prepared at low heat. After dissolving the salts, the solutions are cooled and topped up to 500 ml with a 2.5 M solution of sulfuric acid, previously placed in a volumetric flask of 1 liter. The solution in the flask is stirred and made up to the mark with distilled water. The reagent is stored in a dark glass beaker.

Preparation of reagent B. On the day of analysis, weigh 1,0000 g of ascorbic acid on laboratory balances and dissolve it in 170 ml of reagent A, previously placed in a 1-liter volumetric flask, the volume is adjusted to the mark with distilled water and mixed thoroughly.

Preparation of calibration solutions. First, an initial standard solution of potassium dihydrogen phosphate with a concentration of 0.1 mg 0.1 mg P_2O_5/ml is prepared by dissolving a weighed portion of potassium dihydrogen phosphate in a 0.2 M solution of perchloric acid. A working scale of standard solutions is prepared from this solution.

Determination of mobile phosphorus. To determine phosphorus, 5 ml of an water soil extract (or the required amount of a standard solution) is taken with a pipette, transferred to a 100 ml volumetric flask and added to the mark of reagent B. 10 minutes after coloring the solution, its light absorption is determined on SF-46 in a cuvette layer of 10 mm relative to the reference solution at λ = 670 nm.

The concentration of phosphorus in the samples is determined by a pre-built calibration graph.

Determination of potassium in the soil.

Preparation of calibration solutions. An initial standard solution with a K_2O concentration of 0.5 mg/ml is prepared by dissolving a sample of K_2O in a 0.2 M solution of hydrochloric acid. From this initial standard solution, a working scale of reference solutions is prepared for constructing a calibration graph.

Preparation of water soil extract. On laboratory balance weigh 10 g of dry soil passed through a sieve with holes of 1 mm, place in a flask of 100 ml and pour 50 ml of 0.2 M hydrochloric acid solution. The contents of the flask are shaken for 1 minute and left for 15 minutes, after which the contents are again thoroughly shaken and filtered through a filter "white tape".

Determination of potassium content. Potassium is determined directly from the prepared extract by taking an aliquot into a 10 ml beaker and photometering it on a flame photometer with a light filter, potassium analytical line at λ = 766.5 and λ = 769.9 nm.

The concentration of potassium in the samples is determined by a pre-built calibration graph.

Determination of the total content of heavy metals in the soil

The determination is carried out by extraction of heavy metals with acids. Mobile acid-soluble forms of metals (Cu, Zn, Mn, Pb) are determined in the extracts of 1M HNO_3 or 1M HCl. From soils 1M nitric acid extracts 90–95 % of heavy metals from their gross content. The ratio of soil to solution is 1:10.

Preparation of calibration solutions. Standard solutions for atomic adsorption measurements are prepared from solutions containing 0.1 g/l Me (Cu, Zn, Mn, Pb) by diluting aliquots of 1.5% wt. HNO_3. Solutions with a lower concentration are prepared by diluting the initial solution.

Preparation of water soil extract. A soil sample weighing 10.0 g is weighed on laboratory balance, transferred to a 250 cm^3 conical flask, and 50 cm^3 M HNO_3 is added. The suspension is shaken for 1 hour or left for storage for a day in a flask with a closed stopper. The suspension is filtered through a “white tape” filter, pre-washed with 1 M HNO_3. Before filtration, the suspension is mixed and completely transferred to the filter. The content of heavy metals in the obtained extract is determined by the atomic adsorption method.

Determination of heavy metals content. Turning on the lamp with a hollow Me (Cu, Zn, Mn, Pb) cathode on the monochromator of the atomic adsorption spectrometer, display the analytical line of the corresponding Me. Measure the light absorption of calibration solutions or the studied water soil extract.

The concentration of heavy metals in the samples is determined according to pre-built appropriate calibration graphs.

The obtained results are processed using standard mathematical methods.

Results

In the work, 4 soil samples were taken for analysis, respectively, on the 5th, 15th, 25th and 35th day of the study, which contained the studied masks.

The obtained results are presented in Fig. 1–11.

The dependence of changes in soil pH with the addition of appropriate amounts of tap water, hydrochloric acid, alkali NaOH in a container with the studied masks is shown in Fig. 1.

Fig. 2–5 represent the dependences of heavy metals content (Mn, Cu, Zn, Pb) on the study time for Mask 1, Fig. 6–9 – dependences of heavy metals content (Mn, Cu, Zn, Pb) on the study time for Mask 2 of taking into account the pH medium.

Migration in the soil of mobile forms of phosphorus (Fig. 10) and potassium (Fig. 11) in these soil samples was also determined.

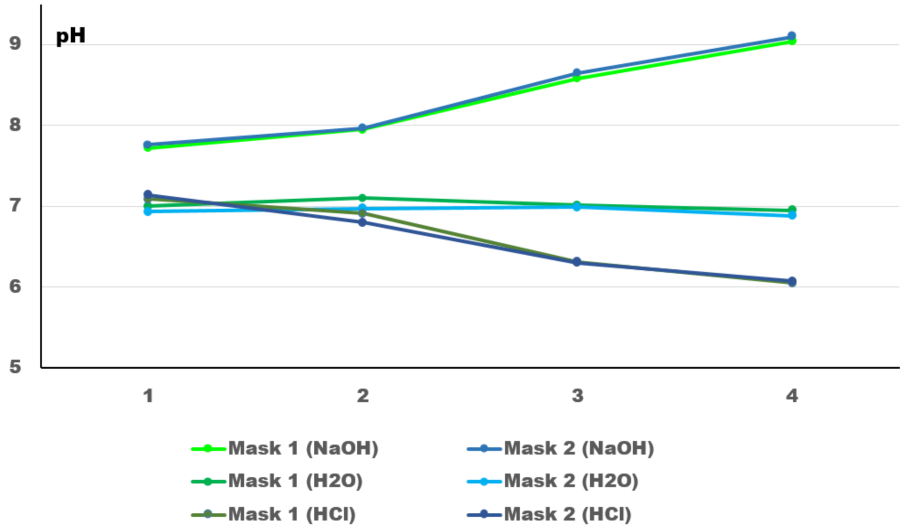

Fig. 1. Soil pH values containing Mask 1 and Mask 2 under acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil conditions on on day 5 (1), 15 (2), 25 (3) and 35 (4) days of the study

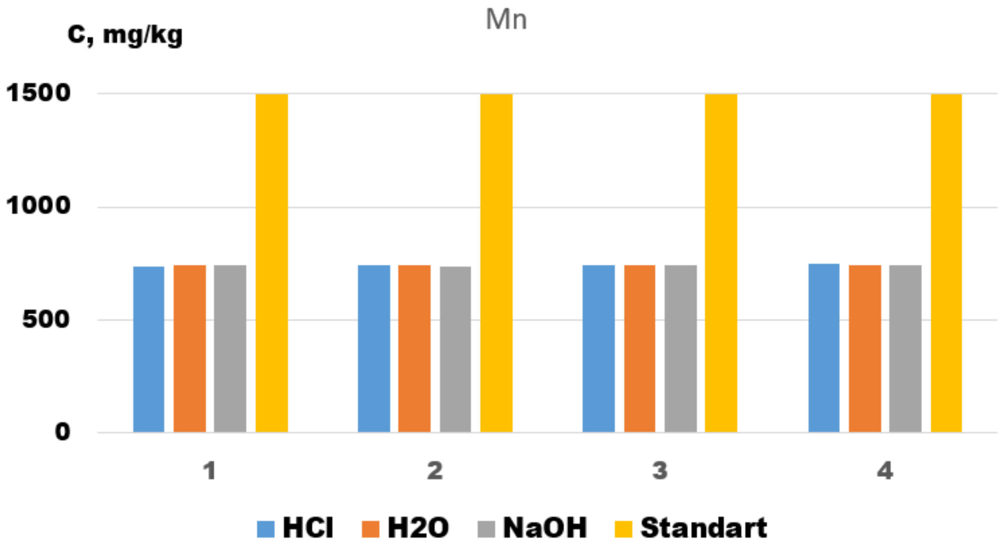

Fig. 2. Manganese content in soil containing Mask 1 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study, and normative value (Standart)

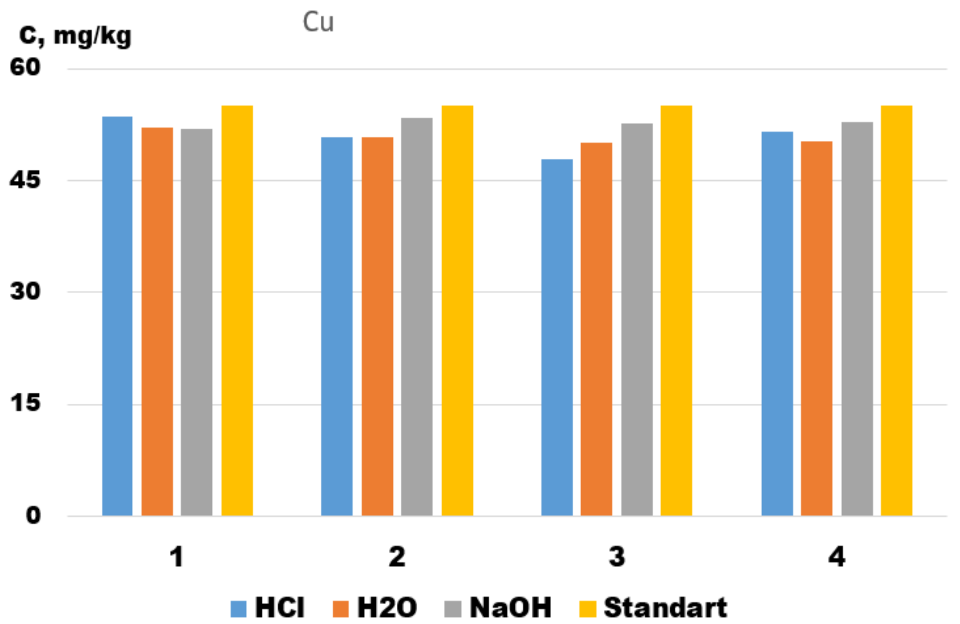

Fig. 3. Copper content in soil containing Mask 1 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study, and normative value (Standart)

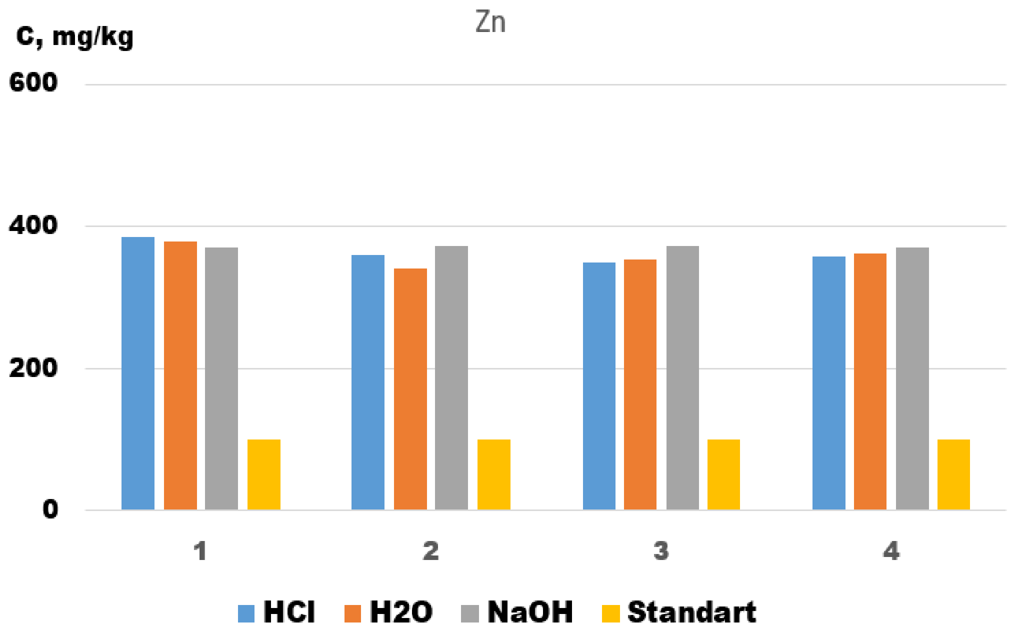

Fig. 4. Zinc content in soil containing Mask 1 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study, and normative value (Standart)

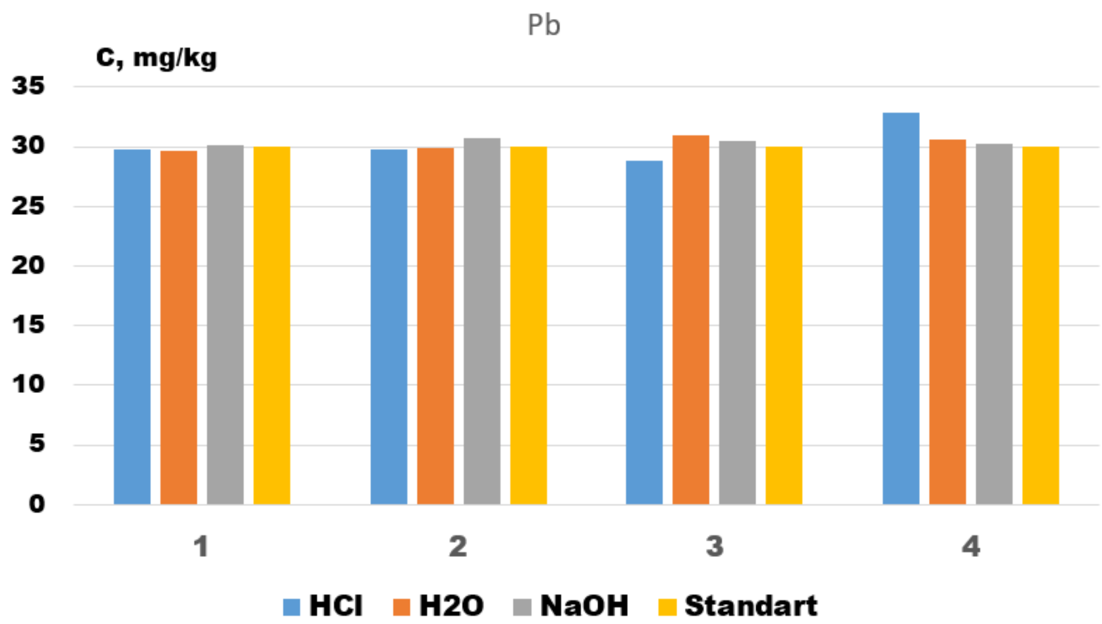

Fig. 5. Lead content in soil containing Mask 1 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on 5 (1), 15 (2), 25 (3) and 35 (4) days of research, and normative value (Standart)

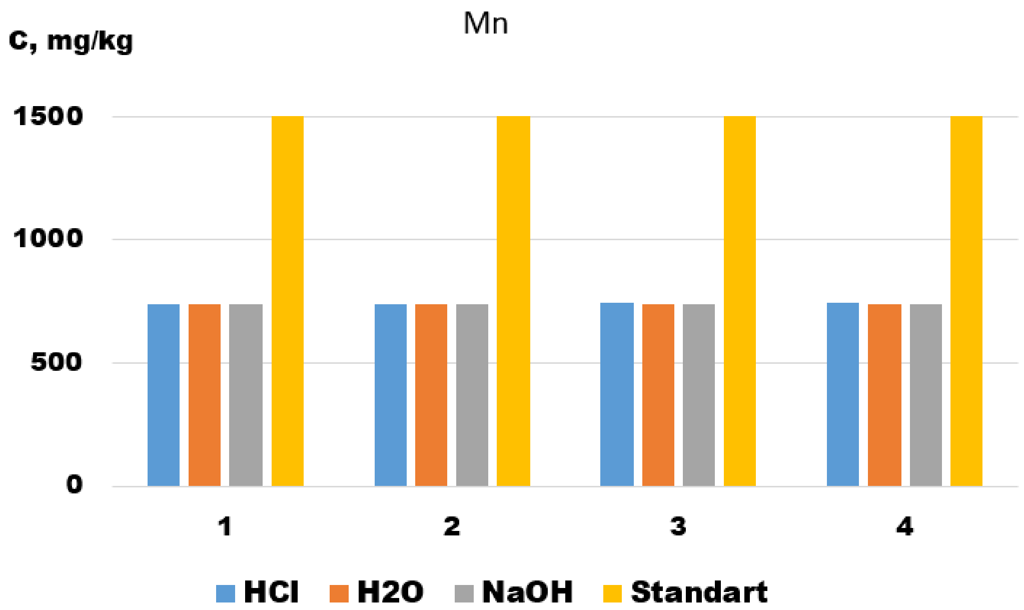

Fig. 6. Manganese content in soil containing Mask 2 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study, and normative value (Standart)

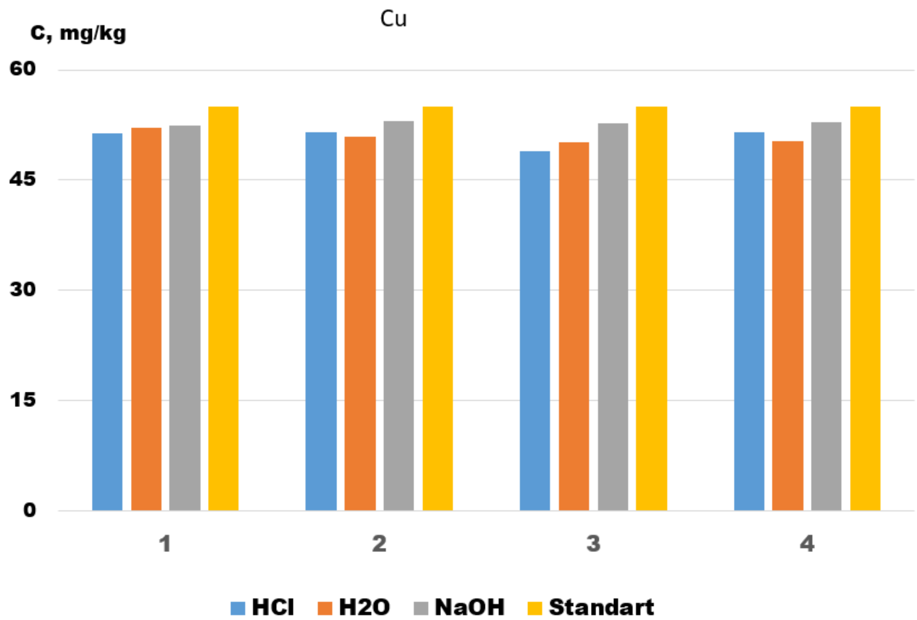

Fig. 7. Copper content in soil containing Mask 1 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study, and normative value (Standart)

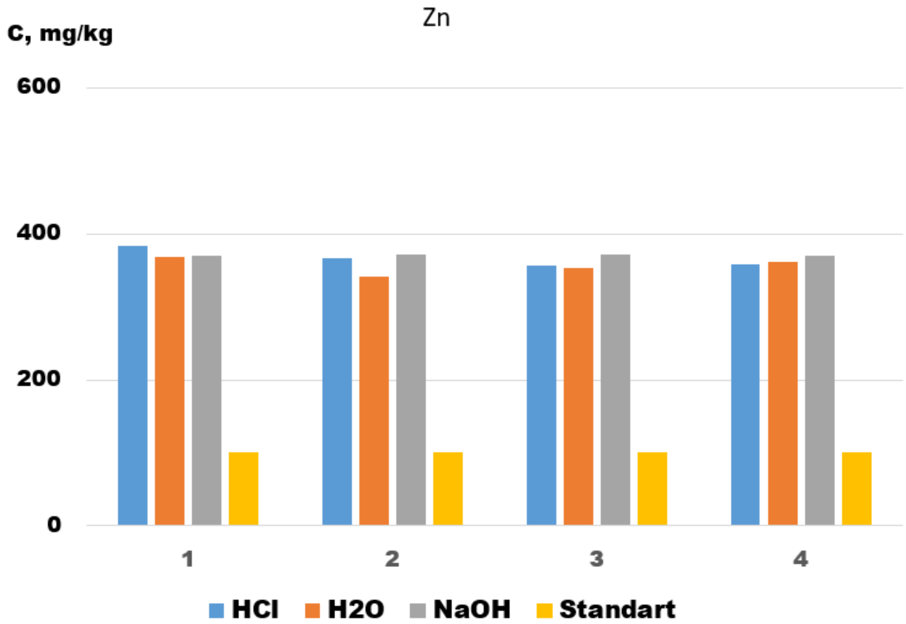

Fig. 8. Zinc content in soil containing Mask 2 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study, and normative value (Standart)

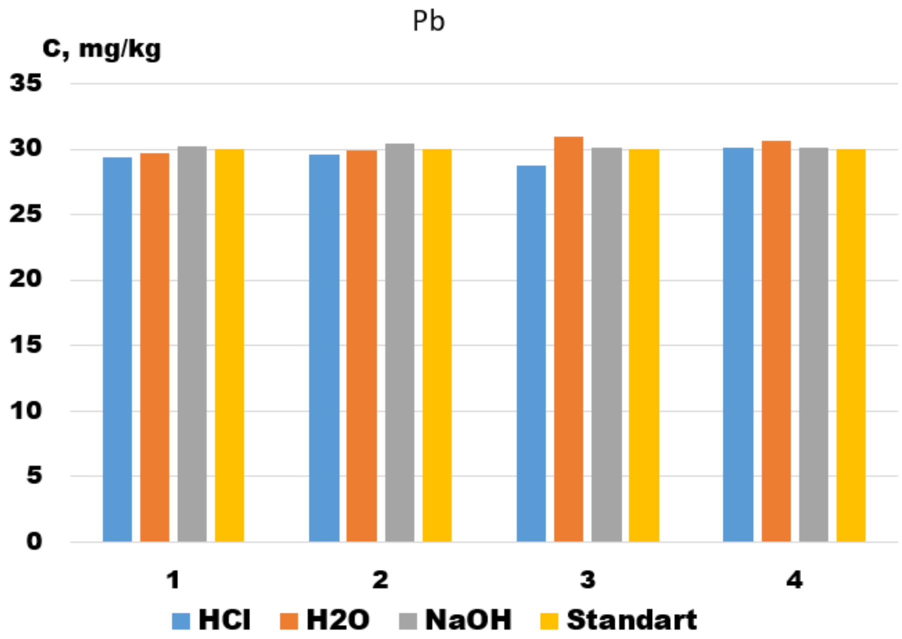

Fig. 9. Lead content in soil containing Mask 2 under conditions of acidified (HCl), neutral (H_2O) and alkaline (NaOH) soil on 5 (1), 15 (2), 25 (3) and 35 (4) days of research, and normative value (Standart)

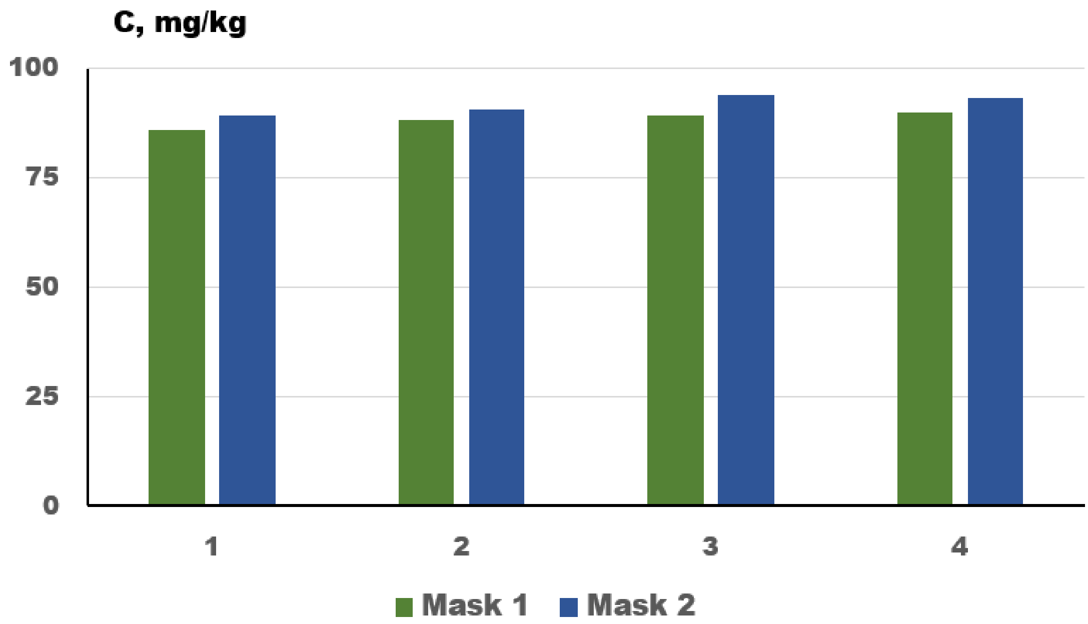

Fig. 10. Potassium content in soil containing Mask 1 and Mask 2 on day 5 (1), 15 (2), 25 (3) and 35 (4) of the study

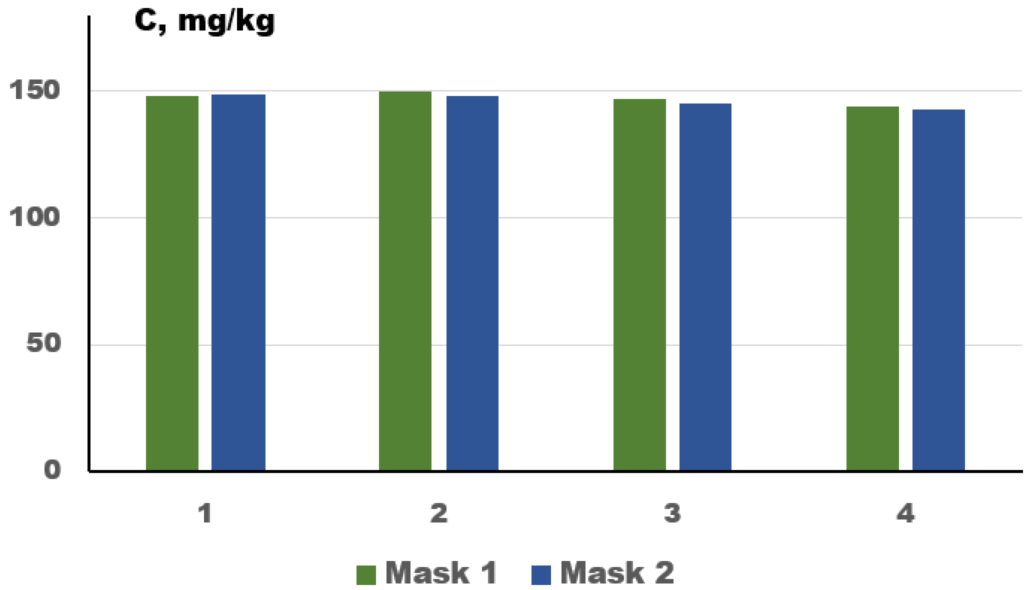

Fig. 11. The content of mobile forms of phosphorus in the soil containing Mask 1 and Mask 2, on the 5th (1), 15 (2), 25 (3) and 35 (4) day of the study

The values of the correlation coefficients of the calibration straight lines for the determination of heavy metals, potassium and phosphorus are presented in table 1.

Table 1. Correlation coefficients of the calibration straight lines for the determination of heavy metals, potassium and phosphorus

Element	Mn	Cu	Zn	Pb	P	K
Correlation coefficient of the calibration straight line, R^2	0.9944	0.9937	0.9986	1.000	0.9982	0.9967

Discussion

The short - term migration of heavy metals from two types of masks into the soil, as well as the content of mobile forms of phosphorus and potassium in the soil are investigated. To take into account possible changes in pH in the environment, the study was carried out in model environments, which were alkaline, acidified and neutral soil samples.

Two types of protective masks were used as research objects: disposable masks from Abifarm (Herbal Fresh), consisting of 2 layers of material "spunbond + meltblown" with essential oils (Mask 1), and disposable masks from Meddins, which consist of of three layers of material "spunbond + meltblown + spunbond" (Mask 2). These materials are made of polypropylene, the difference in physical characteristics is due to the technology of their production.

The experiment is designed to take into account the specifics of the environment in which used protective face masks may fall. In particular, portions of tap water, hydrochloric acid and alkali solutions were added to the contaners containing Mask 1 and Mask 2 in the soil.

Changes in soil pH values for both types of masks during the study period are shown in Fig. 1. Soil pH was investigated by determining the pH of water soil extracts.

As can be seen from the data obtained (Fig. 1), the acidity of soils when adding alkali varies from “medium alkaline” to “strongly alkaline” and, when adding acid, from “neutral” to “nearly neutral” [37] for both types of masks. Differences in pH values between different types of masks are not observed.

In the determination of heavy metals in soils, the atomic absorption method is used, which is often used to determine them in various objects of natural and man-made environment [38]. Data on the maximum allowable concentrations of these metals in soil were used as normative values [37].

Fluctuations in the heavy metals content are characterized by multidirectional dependences when the pH of the medium changes. It is impossible to state unequivocally about the obvious tendency to leach depending on the pH of the solution, neither in the case of Mask 1 (Fig. 2–5), nor in the case of Mask 2 (Fig. 6–9).

Thus, in the case of Manganese (Fig. 2, 6) the effect of soil pH and sampling time does not affect the results of studies, the values do not exceed the norm.

For Copper (Fig. 3, 7) and lead (Fig. 5, 9) there is a different behavior in acidic and neutral environments for Mask 1 and Mask 2. Minor fluctuations in their content in different environments can be associated with the leaching rate, and with the error of the AAS method itself [39, 40]. Exceedances of the normative value are observed for Lead in one case for Mask 1 (Fig. 5) and in two cases for Mask 2 (Fig. 9), although they do not exceed the allowable errors of AAS. The content of copper in soils does not exceed the normative value.

For Mask 1 and Mask 2, there is an excess of zinc content compared to the standard (Fig. 4, 8). It is possible to note faster (at stage (1)) its leaching into the soil in an acidic environment for both types of masks. There is also a slight decrease in its content in an acidic environment.

The mobile forms of phosphorus and potassium in the soil (Fig. 10, 11) are also determined in the work.

Flame photometry is used to determine alkali and alkaline earth metals [41]. This method was used to determine potassium in soil samples. To determine phosphorus, a spectrophotometric method was used, which allows to determine both metals [42] and non-metals [43].

As can be seen from the data obtained (Fig. 10), there is a slight increase in potassium in the soil for both types of masks over time, which may be due to impurities of potassium in water solutions added to the soil to create a pH.

Assuming that soluble phosphorus compounds are present in the soil, their slight decrease (Fig. 11) may be due to the formation of insoluble phosphates with heavy metals that can be washed out of both types of masks under study.

The obtained results indicate the ambiguity of the short-term effect of protective face masks on the condition of the soil, even with varying pH. In particular, during the study period, variations in the content of heavy metals Cu, Zn, Mn, Pb in the soil may be associated with both research errors and have anthropogenic origin, which requires further study.

Conclusions

Thus, it is possible to note the significant interest and concern of the world community in the issues of PPE, and, first of all, protective face masks that are released into the environment as a result of the COVID-19 pandemic. Huge amounts of protective masks are released into the environment, cluttering the aquatic environment, coast and soil. There is a need to find methods of disposal, recycling and management strategies for the management of this group of waste.

It is noted that in addition to plastic and microplastics, PPE and protective face masks are a source of organic and inorganic substances that enter the environment and have a negative impact on biota.

The short-term effect of two types of protective face masks on soils with varying soil pH from “nearly neutral” to “strongly alkaline” in terms of heavy metals content, mobile forms of phosphorus and potassium was analyzed.

There is a similarity in the dynamics of fluctuations in the heavy metals content in the soil for both types of masks, depending on the study period and the soil pH.

The obtained values of the heavy metals content do not exceed the standards of the content of these metals in the soil within the error of the AAS method, with the exception of Zinc.

It should be noted that the results of research indicate the ambiguity of the short-term effect of protective face masks on soil, even with varying pH. In particular, during the study period, variations in the content of heavy metals Cu, Zn, Mn, Pb in the soil may be associated with both research errors and have anthropogenic origin, which requires further study.

References

[1] V.V. Strelets, V.M. Loboichenko, N.A. Leonova, R.I. Shevchenko, V.M. Strelets, A.V. Pruskyi, O.V. Avramenko, Comparative assessment of environmental parameters of foaming agents based on synthetic hydrocarbon used for extinguishing the fires of oil and petroleum products, SOCAR Proceedings. Special Issue No. **2** (2021) 001–010.

[2] Dadashov, V. Loboichenko, A. Kireev, Analysis of the ecological characteristics of environment friendly fire fighting chemicals used in extinguishing oil products. Pollution Research. **37(1)** (2018) 63–77.

[3] T.S. Vovchuk, J.L. Wilk-Jakubowski, V.M. Telelim, V.M. Loboichenko, R.I. Shevchenko, O.S. Shevchenko, N.S. Tregub, Investigation of the use of the acoustic effect in extinguishing fires of oil and petroleum products, SOCAR Proceedings. Special Issue No. **2** (2021) 024–031.

[4] A. Levterov, Acoustic research method for burning flammable substances, Acoustical Physics. **65(4)** (2019) 444–449.

[5] K. Mygalenko, V. Nuyanzin, A. Zemlianskyi, A. Dominik, S. Pozdieiev, Development of the technique for restricting the propagation of fire in natural peat ecosystems, Eastern-European Journal of Enterprise Technologies. **1(10–91)** (2018) 31–37.

[6] Y. Abramov, O. Basmanov, J. Salamov, A. Mikhayluk, O. Yashchenko, Developing a model of tank cooling by water jets from hydraulic monitors under conditions of fire, Eastern-Euroean Journal of Enterprise Technologies.**1(10-97)** (2019) 14–20.

[7] Semko, M. Beskrovnaya, S. Vinogradov, I. Hritsina, N. Yagudina, The usage of high speed impulse liquid jets for putting out gas blowouts, Journal of Theoretical and Applied Mechanics (Poland). **3** (2017) 655–664.

[8] Kovalov, Y. Otrosh, O. Ostroverkh, O. Hrushovinchuk, O. Savchenko, Fire resistance evaluation of reinforced concrete floors with fire-retardant coating by calculation and experimental method, E3S Web of Conferences. **60** (2018) 00003.

[9] N. Rashkevich, R. Shevchenko, I. Khmyrov, A. Soshinskiy, Investigation of the influence of the physical properties of landfill soils on the stability of slopes in the context of solving civil security problems, Materials Science Forum. **1038** (2021) 407–416.

[10] V. Loboichenko, K. Zakomorna, O. Ilinskyi, N. Leonova, A. Malko, R. Shevchenko, Investigation of the Content of Heavy Metals in Water Sources of Kharkiv City, Ukraine, Current applied science and technology. **22(2)** (2022) 1–14.

[11] V. Loboichenko, V. Strelec, The natural waters and aqueous solutions express-identification as element of determination of possible emergency situation, Water and Energy International. **61/RNI(9)** (2018) 43–51.

[12] M. Divizinyuk, N. Kasatkina and B. Melnyk, The Use of Electrical Monitoring and Surveillance Systems to Prevent Emergencies of a Terrorist Nature (on the Example of Motor Vehicles), 2019 IEEE 20th International Conference on Computational Problems of Electrical Engineering (CPEE) (2019) 1– 4.

[13] da Costa JP, The 2019 global pandemic and plastic pollution prevention measures: Playing catch-up, Sci Total Environ. 774 (2021) 145806. doi:10.1016/j.scitotenv.2021.145806.

[14] J. Ammendolia, J. Saturno, A.L. Brooks, S. Jacobs, J.R. Jambeck, An emerging source of plastic pollution: Environmental presence of plastic personal protective equipment (PPE) debris related to COVID-19 in a metropolitan city, Environ Pollut. **269** (2021) 116160.

[15] L. Patrício Silva, A. Tubić, M. Vujić, A.M.V.M. Soares, A.C. Duarte, D. Barcelò, T. Rocha-Santos, Implications of COVID-19 pandemic on environmental compartments: Is plastic pollution a major issue? Journal of Hazardous Materials Advances. **5** (2022) 100041.

[16] M.S. Haque, S. Sharif, A. Masnoon, E. Rashid, SARS-CoV-2 pandemic-induced PPE and single-use plastic waste generation scenario, Waste Manag Res. **39** (1_suppl) (2021) 3–17.

[17] J.E. Celis, W. Espejo, E. Paredes-Osses, S. A. Contreras, G. Chiang, P. Bahamonde, Plastic residues produced with confirmatory testing for COVID-19: Classification, quantification, fate, and impacts on human health, Science of the Total Environment. **760** (2021) 144167.

[18] F.P. De Albuquerque, M. Dhadwal, W. Dastyar, S.M.M. Azizi, I. Karidio, H. Zaman, B.R. Dhar, Fate of disposable face masks in high-solids anaerobic digestion: Experimental observations and review of potential environmental implications, Case Studies in Chemical and Environmental Engineering. **3** (2021) 10008.

[19] M.B. Haddad, G.E. De-la-Torre, M.R. Abelouah, S. Hajji, A.A. Alla, Personal protective equipment (PPE) pollution associated with the COVID-19 pandemic along the coastline of Agadir, Morocco, Sci Total Environ. **798** (2021) 149282.

[20] Tadele Assefa Aragaw, Surgical face masks as a potential source for microplastic pollution in the COVID-19 scenario, Marine Pollution Bulletin. **159** (2020) 111517.

[21] R. Akhbarizadeh, S. Dobaradaran, I. Nabipour, M.Tangestani, D. Abedi, F. Javanfekr, F. Jeddi, A. Zendehboodi, Abandoned Covid-19 personal protective equipment along the Bushehr shores, the Persian Gulf: An emerging source of secondary microplastics in coastlines, Marine Pollution Bulletin. **168** (2021) 112386.

[22] M. Ardusso, A.D. Forero-López, N.S. Buzzi, C.V. Spetter, M.D. Fernández-Severini, COVID-19 pandemic repercussions on plastic and antiviral polymeric textile causing pollution on beaches and coasts of South America, Science of The Total Environment. **763** (2021) 144365.

[23] M.R.J. Rakib, G.E. De-la-Torre, C.I. Pizarro-Ortega, D.C. Dioses-Salinas, S. Al-Nahian, Personal protective equipment (PPE) pollution driven by the COVID-19 pandemic in Cox's Bazar, the longest natural beach in the world, Mar Pollut Bull. **169** (2021) 112497.

[24] T.A. Aragaw, G.E. De-la-Torre, A.A.Teshager, Personal protective equipment (PPE) pollution driven by the COVID-19 pandemic along the shoreline of Lake Tana, Bahir Dar, Ethiopia, Science of the Total Environment. **820** (2022) 153261.

[25] Pengfei Wu, Jiangpeng Li, Xiao Lu, Yuanyuan Tang, Zongwei Cai, Release of tens of thousands of microfibers from discarded face masks under simulated environmental conditions, Science of the Total Environment. **806** (Part 2) (2022) 150458.

[26] Jin Il Kwak, Youn-Joo An, Post COVID-19 pandemic: Biofragmentation and soil ecotoxicological effects of microplastics derived from face masks, Journal of Hazardous Materials. **416** (2021) 126169.

[27] K. Selvaranjan, S. Navaratnam, P. Rajeev, N. Ravintherakumaran, Environmental challenges induced by extensive use of face masks during COVID-19: A review and potential solutions, nvironmental Challenges. (2021). **3**. 100039.

[28] N.V. Rashkevich, V.M. Loboichenko, N.O. Leonova, The used means of personal protective equipment is a dangerous component of solid waste, Collection XIII International Scientific and Methodological Conference, 147 International Scientific Conference of the European Association for Security (EAS) «HUMAN SAFETY IN MODERN CONDITIONS» Kharkiv, Ukraine, December 2–3, (2021) 64-66 [in Ukrainian].

[29] A.L. Patrício Silva, J. C. Prata, A. C. Duarte, D. Barcelò, T. Rocha-Santos, An urgent call to think globally and act locally on landfill disposable plastics under and after covid-19 pandemic: Pollution prevention and technological (Bio) remediation solutions, Chemical Engineering Journal. **426** (2021) 131201.

[30] S.S. Siwal, G. Chaudhary, A.K. Saini, et al, Key ingredients and recycling strategy of personal protective equipment (PPE): Towards sustainable solution for the COVID-19 like pandemics, J Environ Chem Eng. **9(5)** (2021) 106284.

[31] Kuan Shiong Khoo, Lih Yiing Ho, Hooi Ren Lim, Hui Yi Leong, Kit Wayne Chew, Plastic waste associated with the COVID-19 pandemic: Crisis or opportunity? Journal of Hazardous Materials. **417** (2021) 126108.

[32] Jun-Qi Zhang, Xiang Wang, Zhen-Yu Yin, Ningyu Yang, Static and dynamic behaviors of granular soil reinforced by disposable face-mask chips, Journal of Cleaner Production. **331** (2022) 129838.

[33] Z. ur Rehman, U. Khalid, Reuse of COVID-19 face mask for the amelioration of mechanical properties of fat clay: A novel solution to an emerging waste problem, Science of the Total Environment. **794** (2021) 148746.

[34] V. Strelets, V. Loboichenko, N. Leonova, R. Shevchenko, V. Telelim, V. Strelets, O. Shevchenko, A. Burmenko, Analysis of the Influence of Anthropogenic Factors of the Urbanized Territory of Poltava Region (Ukraine) on the State of River Water, Ecological Engineering & Environmental Technology. **23(2)** (2022) 185–192.

[35] V.M. Loboichenko, N.O. Leonova, Regarding the study of the influence of the chemical composition of protective masks for medical and non-medical purposes on the environment, All-Ukrainian Scientific Conference "Actual Problems of Chemistry: Research and Prospects" (April 15, 2021). Conference materials. Zhytomyr: Publisher OO Evenok, (2021) 31 [in Ukrainian].

[36] G. Kutralam-Muniasamy, F. Pérez-Guevara, V.C. Shruti, A critical synthesis of current peer-reviewed literature on the environmental and human health impacts of COVID-19 PPE litter: New findings and next steps, J Hazard Mater. **422** (2022) 126945.

[37] Methods of agrochemical certification of agricultural lands / Ed. S.M. Ryzhuk, M.V. Lisov, D.M. Bentsarovsky. Kiyiv, 2003. [in Ukrainian].

[38] M.Tüzen, Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry, Microchemical Journal. **74(3)** (2003) 289–297.

[39] Purwanto, C. Supriyanto, P. Samin, The Validation of Atomic Absorption Spectrometry (AAS) Method for the Determination of Cr, Cu and Pb, In Sri Jauhari SDwi Wahini Nurhayati, Dwi Wahini Nurhayati, & Tjipto Sujitno, BA. (Eds.). Proceedings of the Scientific Meeting and Presentation on Basic Research in Nuclear of the Science and Technology part II: Nuclear Chemistry and Process Technology. Indonesia: National Nuclear Energy Agency. (2007) 151–158.

[40] 4.3 B: Atomic Absorption Spectroscopy (AAS). Online: https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/04%3A_Experimental_techniques/4.03%3A_Elemental_Analysis/4.3B%3A_Atomic_Absorption_Spectroscopy_(AAS).

[41] P. Banerjee, B. Prasad, Determination of concentration of total sodium and potassium in surface and ground water using a flame photometer, Applied Water Science. **10** (2020) 113.

[42] Drozd, N. Leonova, Spectrophotometric Determination of Ni2+, Co3+, Fe2+, Cu2+ Concentrations with 1-(2-Pyridylazo)-2-Naphthol in Aqueous-Micellar Medium Based on two Intensive Parameters, Chemistry & Chemical Technology. **8(2)** (2014) 129–134.

[43] A.V. Drozd, V.M. Loboichenko, T.S. Tishakova, Spectrophotometric determination of iodides by the products of fluorescein halogenation using electrochemical oxidation, Journal of Analytical Chemistry. **66** (2011) 131–134.

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Drilling Waste Disposal Technology Using Soil Cement Screens

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Abstract. Known technological solutions for well drilling waste utilization are analyzed. The technological decision of the device of storage of drilling waste from soil-cement elements with the device of a covering from soil-cement is offered. It is proposed to fill the repository with waste in layers of drilling mud, site soil, using a layer of composition for neutralization with the use of ash burning wood residues. The composition is proposed to be prepared near storage facilities. It is proposed to make the neutralizing composition periodically in the sludge storage as they are filled. In the case of a high level of sludge contamination with petroleum products, sorbents are added in addition to filling the storage. The thickness of the layers is chosen based on optimal humidity. It is offered to add ash from the Mykolayiv thermal power plant in the amount of 5 wt.% By weight of cement when installing the walls and covering the sludge storage from soil cement. It was found that with increasing the shelf life of samples in water to 270 days increases the average compressive strength of soil cement samples without additives and with the addition of the appropriate percentage of fly ash by more than 7 %.

Introduction

Construction of deep wells, which is an integral part of oil and gas exploration and production. This creates a significant man-made load on the geological environment. Due to the imperfection of well construction processes, dangerous geodynamic processes are developing. A large number of toxic chemical elements and compounds enter the near-surface areas of the hydrosphere and lithosphere [1, 2]. One of the priorities of drilling is to preserve the natural state of the environment as much as possible. Drilling rigs are known to be at high environmental risk. Therefore, the impact on the components of the environment during the construction of wells is possible not only as a result of emergencies, but also under normal conditions of the production process.

The most accessible way to eliminate drilling waste and operate wells is to bury them. Waste disposal is practiced in specially designated areas. This is practiced in deep underground horizons, in earth storage facilities directly on the drilling site.

The size of the barns is determined by the project and must correspond to the amount of waste drilling [1]. If drilling mud gets into the natural environment, it can upset the balance of ecosystems. It contains the following potentially dangerous components: hydrocarbons; heavy metals; components present in drilling fluids.

To prevent drilling waste from entering the soil and groundwater, it is necessary to provide an engineering system of organized waste collection. To do this, special tanks are installed on the territory of the drilling rig or earthen pits are built in the mineral soil - sludge barns.

A feature of the design of sludge barns is the need to waterproof the walls and bottom. Its absence leads to filtration of barn contents into groundwater and subsequent migration of pollutants. Therefore, the problem of liquidation of sludge barns and further reclamation of lands on the territory of drilling rigs is quite relevant at present.

In a number of regions, the bottom and walls of storage facilities are used for clay - artificial filling of cavities and large cracks in rock or soil with clay. This method was proposed and implemented in the USSR in 1928. However, clay does not give the desired result, in addition, this method is quite time consuming and non-technological.

A more environmentally friendly way of disposing of drilling waste involves the construction of ditches in the ground with waterproofing. Waterproofing of such sludge storages protects groundwater from the penetration of toxic waste, provides disinfection and safe disposal of recycled masses. Metal sheets, synthetic film, reinforced concrete slabs, bentonite mats, wooden boards with bituminous coating or compositions based on clay, lime and cement are used for waterproofing [3].

There is a method of waterproofing sludge barns with the use of geotextile membranes. According to this technology, a sand cushion is created on the bottom and walls of the sludge storage, it is compacted and covered with geotextile. After that, a waterproofing membrane is laid, which in some cases is additionally protected by a layer of rubble or geosynthetics. Despite the complexity, the work is performed quickly due to the lightness and flexibility of the roll materials, but the force can damage the membranes.

The main disadvantage of geomembranes as waterproofing in the construction of sludge pantry is the multi-stage installation.

Also known is the technology of using low-viscosity injectable hydroactive resin of hydrophilic type AQUIDUR ES-P. Depending on the amount of water, this resin can form both a gel and an elastic rubber-like material with a closed pore structure. After drying, it remains a rubber-like elastic material with hydrophilic properties. When the material interacts with the aqueous suspension forms a filled gel. When interacting with moist soil - elastic composite.

G.P. Bochkarev recommends arranging waterproofing in two stages. At the first stage, a grout-based mortar is applied to the walls and bottom of the barn. In the second stage, after curing the first layer, a layer based on polyacrylamide and cement is applied to reduce the likelihood of cracks [2].

O.A. Mamayevska describes the use of multilayer waterproofing, which consists of a layer of sand, waterproofing layer, underlying, compacted base soil. According to the experience of design, the application of a protective layer of sandy soil can be accompanied by a number of difficulties: insufficient stability of the soil on the slopes, external natural and climatic factors. The use of a sand cushion, a large enough volume, is not advisable and provides only some protection of the waterproofing layer from mechanical damage by the excavator bucket when mixing the cement mass. The thermal conductivity of sand is quite good, so this pillow is not insulating. [4]

As an alternative to the sand cushion, you can use more effective methods of integrated protection with waterproofing materials, which is especially important when placing sludge pantries on permafrost.

K.A. Timofeeva proposes the installation of sludge barn from soil cement using the technology of manufacturing soil-cement elements by drilling technology without excavation [1,3].

According to the proposed technology, wells are drilled around the perimeter of the sludge barn. These wells are filled with soil cement, which is a protective shield against groundwater. [1]. There is also a known method of arranging the bottom of the pit of soil cement, which is mixed separately in a concrete mixer and poured in a continuous layer on the bottom of the barn [3].

These methods of making waterproof screens are time consuming, expensive and over time their effectiveness to resist the chemical action of the components of drilling waste is reduced. Thus, the aim is to propose and justify, improve the technology of drilling waste storage (sludge storage).

Methodology and Research

It is necessary to investigate the creation of such a method of waterproofing storage barns and disposal of drilling waste in the construction of oil and gas wells, which would ensure guaranteed protection of surface, groundwater and groundwater from pollution due to the penetration of harmful drilling waste into the soil. Complete environmental safety of barn drilling and environmental protection. This goal is achieved by performing continuous waterproofing of sludge barns from soil cement.

Soil cement is a mixture of clay soil, cement and water. It is not a simple mechanical mixture, but a system consisting of two very complex in composition and properties of multicomponent systems - cement and soil. The main leading factor in the radical transformation of soil properties is cement, which is a polydisperse and polymeric system that can form a stone-like body after the addition of water.

The construction of the sludge storage is performed as follows. A monolithic vertical anti-filtration curtain of the «soil in the soil» type is constructed from soil-cement elements (figure 1).

The distance between the centers of adjacent elements should be equal to 0.8d (d is the diameter of the soil-cement elements). Soil-cement elements are made by drilling method [8]. The main processes of the technology are mechanical destruction (grinding) of the soil, injection into the soil of the binder (stabilizer) and mixing of the soil with the binder working body of the drilling machine. As a result of mixing and hardening of cement in the soil, a pile with a fixed diameter is formed, which is determined by the size of the mixing blades of the equipment. The binder is fed through holes (nozzles) in the drilling projectile (working body of the drilling machine).

Thus, we obtain cylindrical soil-cement elements with a diameter of 0.3–0.8 m and a length of up to 30 m [1]. The anti-filtration curtain of the «soil in the soil» type of soil-cement elements is deepened into the water resistance to a depth of at least 1 m in order to ensure the absence of filtration. After hardening of soil-cement elements along the perimeter of the sludge storage, up to 60% of the soil mass is excavated [1]. The period of hardening in the moist state lasts 28 days. Over time, the strength and water resistance of soil cement increase.

Filling of sludge storage with drilling waste is carried out after hardening of soil cement. Drilling waste is dehydrated before entering the sludge storage facility.

Dehydration is proposed to be carried out by separation in the centrifugal field of drilling mud in the decanter. The principle of its action is based on the action of centrifugal forces. In the decanter oil sludge in a mixture with heated fresh oil is fed to three-phase decanters, where it is divided into three phases: hydrocarbon, water and mechanical impurities. The separated hydrocarbons are sent for recycling, water - for purification, mechanical impurities, which are enriched with hydrocarbons and contain water, are new waste, the amount of which is much less compared to the amount of primary sludge, but still significant. The advantages of this type of recycling of drilling mud include the ability to reduce waste, as well as reuse part of the water, which is separated from petroleum products in 20 minutes. 28 % by weight of water is separated from the source sludge by centrifugation. Whereas from sludge after freezing and thawing - more than 39 %. Thus, freezing and thawing destabilize the sludge structure and increase the efficiency of its dehydration in model centrifugation conditions. This method is more suitable for mixtures consisting of synthetic organic substances. [5–8]. The thickened phase after dehydration enters the sludge storage.

As the sludge storage is filled, it is filled with waste according to the following technology: a layer of waste about 1 m thick is poured on the bottom of the sludge storage, then a soil layer of the construction site (humidity 4–5 %) up to 1 m is poured on top. loam. Bringing the site stacked in the soil dumps to a humidity of 4–5 % is done by drying it in the open air with periodic stirring and construction over the shelter storage place.

Humidity of dehydrated drilling mud after dehydration by centrifugation and freezing and thawing about 25 %

However, such wastes, even with the addition of a layer of soil, may have a humidity that is different from the optimum. In order to reduce the moisture content of drilling mud, the technology of adding solid fuel combustion ash from thermal power plants (ash from cleaning cyclones) can be used. The problem of accumulation of waste of enterprises, boiler-houses at burning of solid fuel which occupy considerable areas is actual.

The growth of production in the woodworking industry is paying close attention to the technology of burning wet biofuels. Waste from sawmills - bark, sawdust, wood chips (with a humidity of 30 to 65 %) can be used as fuel. In Europe, solid biofuels based on plant biomass (mostly wood) are increasingly displacing fossil fuels (oil, coal, gas) from the heat market.

Repeated tests of incineration of bark, sawdust and mixtures of packaging waste, husks from cereals, lump peat and biological sludge of the woodworking industry mixed with bark and sawdust showed very low emissions of hydrocarbons, polycyclic aromatic hydrocarbons and heavy metals. Thus, measures to protect the environment by reducing greenhouse gas emissions and dust into the atmosphere are implemented in practice. However, in this case, significant amounts of ash waste are generated from the combustion of wood material. This material is environmentally friendly, so it is recommended to use it to reduce the environmental load of buried waste dehydrated drilling mud.

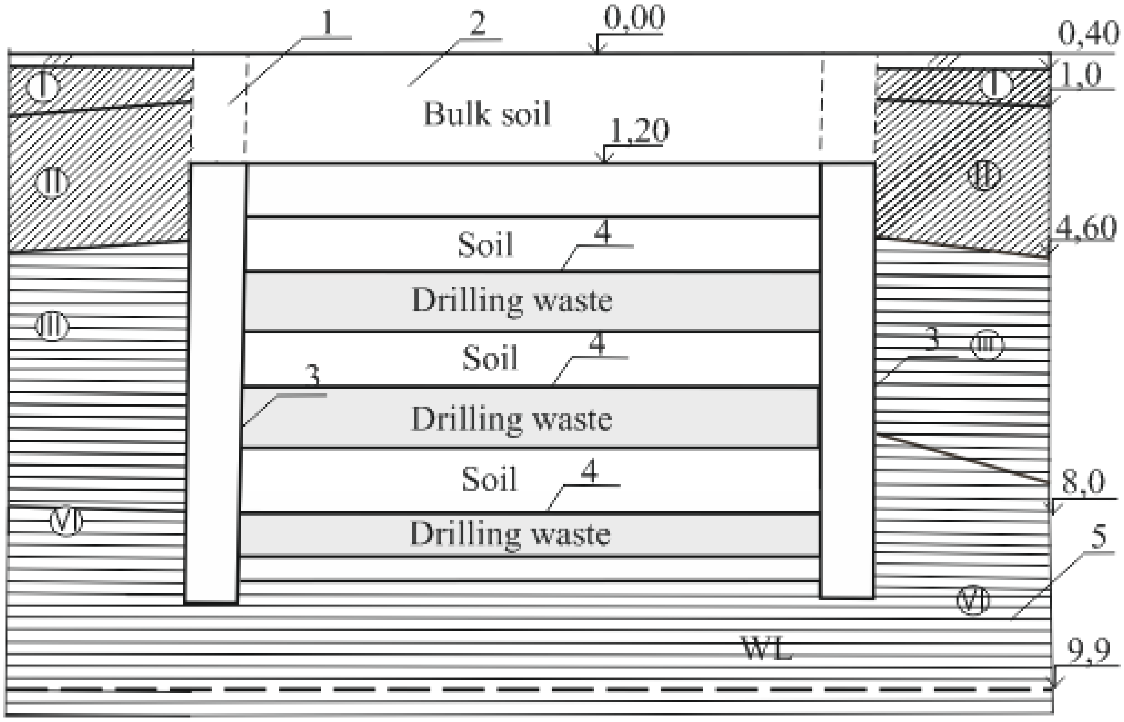

Fig. 1. Type of sludge storage of the offered design: 1 – soil-cement element which can be dismantled; backfilling of the site with soil; 3 – soil-cement element of the sludge storage; 4 – composition for neutralization; 5 – clay soil (water resistance)

There is a method of using waste ash removal of thermal power plants in road construction in order to drain the soil layers (p. 6.4.9 DBN B.2.3-4: 2007) [6].

The amount of additive is from 1.5 to 3 % depending on the type of soil. The authors propose to use ash from burning wood raw materials after cyclones (Fig. 2) in order to reduce the moisture content of waste to achieve their optimal density. Since drilling mud can be classified as heavy loam, its amount is from 1 to 2 % by weight of soil at its moisture content in relative units from the optimum humidity of 1.2 to 1.4.

Fig. 2. General appearance of additives: 1 – ash formed on the surfaces of the heat exchanger of the boiler unit sifted on a sieve with a hole size of 1 mm; 2 – ash from cleaning cyclones

The thickness of the layers is selected and calculated to obtain the optimum moisture content of the sludge and soil mixture. Then perform compaction of sludge and loam layers with rammers. After compaction, the operation is repeated. Compaction of soil layers should be carried out at optimum humidity in order to obtain the maximum coefficient of compaction and placement in the storage of the maximum amount of waste.

The compacted soil is covered with soil cement. The thickness of such a coating is offered 0.5–1 m, depending on the purpose of use of the area where the storage is located.

A significant advantage of the use of soil-cement elements is that the most favorable environment for their arrangement are water-saturated soils, including those located below the groundwater level. Soil cement, despite its high porosity, has an abnormally high water resistance.

Experience has shown that the physicochemical characteristics of loess soils, namely low content of clay particles, alkaline reaction of the medium, low amount of easily soluble salts, easy dispersion in water saturation due to water-soluble bonds between particles - all these features contribute to the use of soil cement . The mechanical characteristics of the soil cement, namely the prismatic strength and the modulus of deformation are provided by the presence of crystallization bonds formed during the hardening of the material. The rate of hardening of soil cement is most affected by ambient temperature. The modulus of deformation depends on the density of soil cement. It is experimentally proved that at the same prismatic strength the deformation modulus is larger for a sample with a higher density.

Consider the technological solutions for the construction of sludge barns (storages) at the Zhuravlyne field. Administratively, the field is located behind outside the settlements in the Valkiv district of Kharkiv region. The nearest settlement is the village of Kovyagi on the south-eastern side at a distance of about 3.5 km.

Wastes from the production of well drilling №7 at the Zhuravlyne field are drilling wastewater and meteorological precipitation water, spent drilling mud, sludge (drilled rock particles) and surplus grouting (cement) solutions. Waste is currently accumulated and stored in earthen containers.

During their temporary storage in the tanks is settling (sedimentation of solid particles) and the formation of a volume of technical water. In the process of drilling a well, settled water (~ 60 %) is reused in the technological process. The calculation of the amount of drilling waste and the volume of sludge barns was carried out in accordance with the methodology set out in COU 73.1-41-11.00.01:2005.

The volumes of sludge barns were determined at the design stage of well construction, based on the estimated volumes of drilling waste with a reserve of $V_{am} = 4000\ m^3$, and the depth of the barns was taken into account the groundwater level at the drilling site. № 7:

a) for dumping of drilled rock and spent solution ($V_{a1} = 3000\ m^3$);

b) for collection and settling of drilling wastewater ($V_{a2} = 1000\ m^3$);

d) for discharge, degassed liquid, through the discharge lines of the ejection equipment ($V = 300\ m^3$).

The depth of barns depends on the groundwater level at a particular site. The depth of sludge barns is taken to be 3.0 m. The distance from the bottom of the barn to the maximum horizon of groundwater must be at least 2 m. The steepness of the barn slopes of 30 degrees is accepted:

According to engineering and geological surveys at the well site № 7, groundwater to a depth of 10.5 m was not recorded.

Sludge barns along the perimeter were embanked with soil at least 0.5 m high. The following sludge barn construction was used, where the first barn is constructed in such a way that excess drilling wastewater from sewage ditches is poured into the second barn to settle water. The settled water flows through a pipe below the liquid level of the second barn into the barn for collecting purified water. For reuse, purified water is pumped through a line to the tank.

The dimensions of sludge barns (including slopes) are based on the estimated amount of drilling waste.

The volume of the sludge barn was projected at 638 m^3 (Fig. 2). Drilling waste was disposed of after separation of the liquid fraction. In this case, the volume of the sludge storage is reduced to 403 m^3 if the aqueous phase is separated from the drilling fluid. In this case, it is accepted that the settling can remove 37 % of the aqueous phase.

The following dimensions of sludge barns have been introduced and arranged (Table 1).

Table 1. Dimensions of sludge barns

List of barns	Volume of the barn, [m^3]	Depth of the barn, [m]	The bottom of the barn, [m×m]	The area of the bottom of the barn is [m×m]
1 barn – sludge	1900	3.0	37×10	370
2 barns – for collecting and defending drilling wastewater	1408	3.0	34×7	238

Before the start of work on the drilling site of well № 7 of the Zhuravlyne field within the Derkachiv-Voitenko license area, field engineering and geological surveys were conducted. To establish an engineering geological section and take soil samples, 5 wells with a depth of 10.5 m and 1 well with a depth of 3.0 m were drilled. During drilling, soil samples were taken for laboratory determination of physical and mechanical properties of soils.

In terms of engineering and geological surveys, up to a depth of 10.5 m, five engineering and geological elements have been identified, and up to a depth of 25.5 m, three more engineering and geological elements (IGE):

IGE-1a – soil-vegetation layer, chernozem, layer thickness up to 0.4 m. Opened by all wells.

IGE-1b – brown solid loam, with plant roots, the presence of frequent molehills. Layer thickness up to 1.0 m. Opened by all wells.

IGE-2 – light brown loam solid, woody with carbonate veins breed. Layer thickness from 3.1 m to 3.3 m. Opened by all wells.

IGE-3 – brown clay, yellow-brown solid, carbonate-containing. Power layer from 3.4 m to 3.5 m. Opened by all wells.

IGE-4 – hard brown clays. Layer thickness from 2.3 m to 2.5 m.

Groundwater is opened by wells at depths of 9.6–10.0 m.

The area of the waste storage facility is potentially non-flooded.

Sludge barns are built in soils with filtration coefficients from 7.52.10-4 cm/sec. Solid waste from drilling wells belongs to the fourth hazard class, so taking into account the requirements of SNiP 2.01.28-85, the limit values of filtration should not exceed 10–5 cm/s, it is necessary to insulate the soil.

Rolled polymer-bitumen materials were used as anti-filtration screens for waterproofing of drilling land barns. Today, Ukraine produces roll polymer-bitumen waterproofing – «Krembit» according to TU U B.2.7-00294349.58, Or its analogue, such as «Aquaizol APP PE-2.5». They are resistant to the aggressive action of test media simulating liquid drilling waste. The joints of the canvases were made by surfacing. The edges of the polymer-bitumen material should be removed outside the barn around the perimeter to a width of at least 1.5 m and fixed with a layer of soil to prevent slipping. The magnitude of the soil slope under such a screen is not less than 1:3. In this case, a smooth transition from the bottom surface to the slope.

However, the disadvantage of such screens is the possibility of destruction and not rigid fixation of the coating.

For waterproofing of the barn for the discharge of gassed liquid, the construction of a soil anti-filtration screen from clay soil over the entire area (bottom and walls) of the barn according to SOU 73.1-41-11.00.01: 2005. For barns up to 3 m deep, a soil screen 30 cm thick is quite reliable. After applying the clay screen, the surface of the barn was treated with sodium chloride (NaCl), for which the required amount of salt, the mass fraction of which is 10–15 % by weight, is spread on the prepared area and with the help of a road cutter mixed with soil. Before burying the waste at the drilling site, the waste is neutralized. Neutralization is achieved by accelerating the biodegradation of organic compounds. In the barn sludge is introduced a composition containing phosphogypsum, wood ash and organic fertilizers in such concentrations, the mass fraction of which is:

phosphogypsum – from 2.0 % to 3.0 %, wood ash from 1.0 % to 2.0 %, organic fertilizers from 3.0 % to 5.0 %.

Taking into account the actual volumes of drilling waste, 1734 tons are subject to neutralization. In this case, the required amount of phosphogypsum is 43.35 tons; ash 26.01 tons; organic fertilizers 69.36 tons.

The authors propose to use ash from burning wood residues. This will allow you to dispose of waste and ensure drainage of waste to the required optimum humidity.

The composition is proposed to be prepared near storage facilities, to be made periodically in sludge storage facilities as they are filled. In case of high level of sludge contamination with oil products, sorbents are added in the following quantities per cubic meter of waste when filling the repository: hydrophobic perlite – from 0.1 kg to 0.2 kg, or diatomaceous earth – from 0.2 kg to 0.5 kg , or bentonite powder – from 0.5 kg to 1.0 kg.

The applied sorbent binds petroleum products and prevents them from penetrating the fertile soil layer. Thus, it is planned to bury about 364 m^3 of removed rock, and 690 m^3 of spent flushing fluid and 88 m^3 well test solution. The total amount of bentonite powder required for neutralization of oil pollution is 1.142 tons. The applied layer is plowed with a plow. After that, apply a working layer of soil.

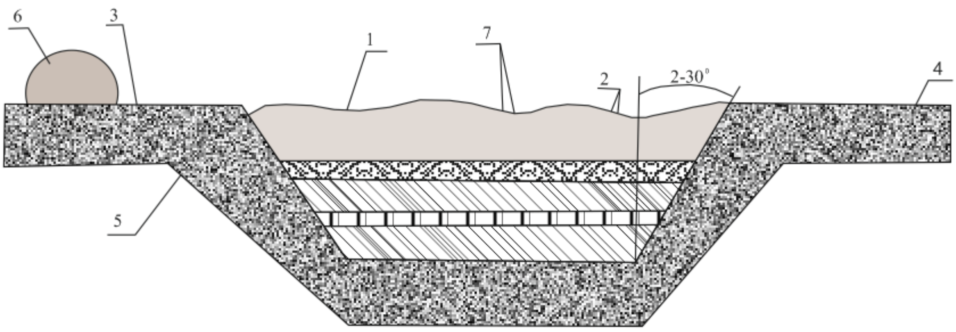

Fig. 3. General view of the existing system of barns for wells № 7 Zhuravlyne field: 1 – bulk soil with a thickness of at least 0.8 m; 2 – sludge; 3 – waterproofing layer; 4 – compacted soil; 5 – soil base; 6 – embankment; 7 – composition of neutralization of drilling mud.

The main dangerous and toxic pollutants when drilling a well № 7 Cranberry deposit are soda ash (Ca_2CO_3), potassium chloride (CSI). Known studies of the effects of these substances on soil-cement samples.

With increasing shelf life of soil cement samples (cylinders h = 15 cm, d = 15 cm) in chemical solutions and water (from 30 days to 270 days) the strength of soil cement for uniaxial compression R increased: from 5.52 to 7.74 MPa (40 %) when kept in tap water H_2O; from 5.21 to 6.85 MPa (31 %) when kept in a 4 % solution of caustic soda; from 4.96 to 6.43 MPa (30 %) when kept in 15.0 % KCl solution [1].

That is, the presence of soda ash (Ca_2CO_3), potassium chloride (CSI) in the drilling mud increases the strength of soil cement for uniaxial compression.

The proposed design of the sludge storage will allow to dispose of wood burning waste and use them as a drying material. It will provide reliable insulation against the ingress of drilling waste into groundwater and soil, because over the years the strength of soil cement is only increasing. It is also proposed to add solid fuel combustion ash (removal ash) when installing soil-cement storage and coating walls in order to improve its strength.

Removal ash is a fine material with a small particle size, which allows it to be used for a number of industries without additional grinding. A characteristic feature of ash is the presence of about 5–6 % of unburned fuel and iron. The slag particles have sizes from 0.2 to 20–30 mm. In furnaces with liquid slag removal, the slag is obtained in granular form [5].

Kovalsky V.P (2014) reports the possibility of introducing 20 % of fine fly ash from thermal power plants into mortars in order to save high-grade Portland cement. In this case, the ash is given the role of mineral microfiller of cement, which increases the plasticity of solutions. The possibility of using in solutions both as a fine additive and as a fine-grained filler has been investigated [10].

Experiments to study the strength of soil-cement samples were carried out with the ash removal of the Mykolayiv thermal power plant. The ash of the Mykolayiv thermal power plant before the experiment was sieved on a 4 mm sieve because the ash contains a significant amount of impurities. The content of inclusions from 1 to 4 mm was up to 40 %. The average humidity of the removal ash was 0.6 %.

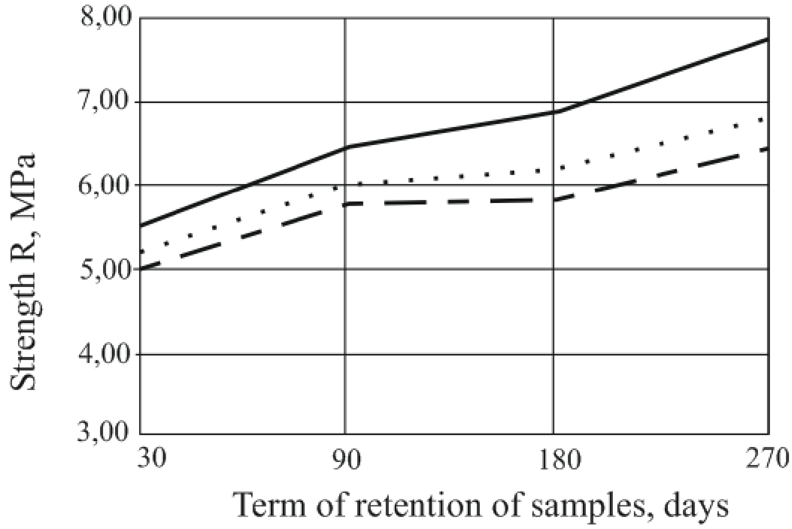

Fig. 4. Dependences of strength of soil cement samples on term and environment of endurance: 1 – water; 2 – Ca_2CO_3; 3 – KCl [1].

The experiment was performed as follows: cement and water in the required amount were mixed to obtain «cement milk». The amount of cement was 20 % by weight of dry soil. Water-cement ratio (W/C) was 1.0. Then, 5 % of the cement ash was added to the resulting solution and mixed. Soil (loam loam) with a moisture content of 14 % was added to the «cement milk» with the addition of fly ash. The mixture was stirred until smooth for at least 5 minutes. Preparation of soil-cement samples in the laboratory was carried out with the approximation of technological conditions [11].

After mixing, the soil-cement mixture was placed in cylindrical molds with a diameter of 2.8 cm and a height of 3.5–4 cm. Prior to the test, the samples were stored immersed in water for 28, 90, 180, 270 days to gain strength.

Table 2. Characteristics of compressive strength of soil-cement samples with the addition of fly ash (aged 28–270 days) at a coefficient of variation, υ

Average compressive strength, MPa	No additives	With the addition of removal ash
		5 %
R_{28}/ υ	2.78/0.30	3.64/0.11
R_{90}/ υ	3.06/0.28	3.91/0.13
R_{180}/ υ	3.295/0.19	4.14/0.27
R_{270}/ υ	3.18/0.10	3.94/0.21

The tests were carried out in accordance with DSTU B B.2.7-214: 2009 as for concrete, taking into account DSTU B B.2.1-4-96. The experiment was performed with 6 samples.

According to the results of research it is established that with increasing the shelf life of samples in water to 270 days increases the average compressive strength of soil cement samples without additives and with the addition of the appropriate percentage of fly ash by 12–17 %. For example, the average compressive strength of soil cement samples with the addition of fly ash 5 wt.% At the age of 270 days increased by 7.6 % compared to the same value at the age of 28 days.

Conclusions

This method of creating a technological solution is relevant in the presence of a waterproof layer at the optimal depth from the surface (8–20 m).

The coating is applied to the drilled sludge thickened to a rigid plastic consistency with the addition of soil from the construction site. The advantages of the design of the sludge storage with the installation of soil-cement coating is the low cost of production due to the use of a waterproof layer of soil as the bottom of the structure. After hardening of the soil cement, the sludge storage cover is covered with a layer of fertile soil. Thus, it is possible to solve the problem of disposal of soil removed during the construction of sludge storage.

It is proposed to fill the sludge storage with a mixture of drilling mud and site soil (in the conditions of Poltava region - refractory loam) with alternating layers. It is also proposed to use a neutralization mixture consisting of phosphogypsum, wood ash and organic fertilizers to neutralize waste and reduce the negative impact on the environment. This mixture will perform the functions of disinfection and drying of the mixture of drilling mud and soil, as the mixture includes ash.

It is proposed to add ash from the Mykolayiv thermal power plant in the amount of 5 wt.% By weight of cement when installing the walls and covering the sludge storage from soil cement. It was found that with increasing the shelf life of samples in water to 270 days increases the average compressive strength of soil cement samples without additives and with the addition of the appropriate percentage of fly ash by more than 7 %.

Reference

[1] K.A. Timofeeva. Soil-cement storages for toxic waste of drilling and operation of oil and gas wells : Abstract. dissertation ... Cand. tech. Sciences: 05.23.02 Poltava. nat. tech. them. Y. Kondratyuk. Poltava, 2016, 22 p.

[2] Method for waterproofing a sludge pit. No. 140153 IPC E02D 29/00, MPC E02D 31/00 Ukraine / G.B. Bochkarev, B.A. Anderson, A.U. Sharipov, D.A. Galimov, S.D. Rudakov - No. SU 1778130; Appl. 07.02.1990; Published 11.30.1992. Bull 1992, № 44, 3 p.

[3] K.A. Timofeeva. Laboratory researches of influence of aggressive components of drilling mud on physical and mechanical characteristics of soil cement. Collection of scientific works (branch mechanical engineering, construction) 1 (40) (2014) 259–267.

[4] O.A. Mamaevskaya, D.A. Akhpolov. Environmental safety in the design of sludge pits// International Institute of Vocational Education Proceedings of the All-Russian Scientific and Practical Conference Actual Issues and Innovative Solutions in the Oil and Gas Industry, Samara 2021, https://inipe.com/conference-2021-ahpolovda/

[5] N.I. Rikusova. Modern methods of processing and utilization of the drilling of oil and gas sverdlovins. Ecological sciences № 1 (20) volume 2 (2014) 130–135 http://ecoj.dea.kiev.ua/archives/2018/1/part_2/29.pdf

[6] DBN B.2.3-4: 2007. ROADS Part I. Design Part II. Construction. Effective from March 1, 2008. Ministry of Regional Development of Ukraine, State Service of Motor Roads of Ukraine (Ukravtodor) 122.

[7] A.M. Ermeev, A.A. Elpidinsky. Dehydration of oil sludge by the method of exposure to low temperatures. Bulletin of the Kazan Technological University, № 10. (2013) 266–268.

[8] A.A. Nesmelov T.V. Grigorieva, R.Kh. Khuzayanov. Preparation of hydrocarbon-containing sludge for biological disposal. Bulletin of the Kazan Technological University, № 14. (2012) 177–181.

[9] S.V. Lanko, V.V. Konyushkov. Boring-mixing technology of soil fixing. St. Petersburg (2020) 52.

[10] V.P. Kovalsky, O.S. Sidlak. Use of tese assembly ash in building materials. Scientific and technical collection “modern technologies 35–40 https:// stmkvb.vntu.edu.ua

[11] M. Zotsenko, O.Mykhailovska, I. Shirinzade, I. Lartseva. Lecture Influence of Fly Ash Additives on Strength Characteristics of Soil–Cement as a Material for Waste Storage Construction**.** Notes in Civil Engineering Conference Paper, 181 (2022) 457–464.

Keyword Index

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