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JOURNAL	World Science
p-ISSN	2413-1032
e-ISSN	2414-6404
PUBLISHER	RS Global Sp. z O.O., Poland

ARTICLE TITLE	CLEANING WATER SURFACE CONTAMINATED WITH LIGHT OIL FRACTION USING A NEW HYBRID SORBENT
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ARTICLE INFO	Molodinashvili Zaza, Kopaleishvili Maka, Gabunia Tinatin, Shatakishvili Tamar, Chikaidze Marina, Razmadze Dali. (2024) Cleaning Water Surface Contaminated With Light Oil Fraction Using a New Hybrid Sorbent. *World Science*. 2(84). doi: 10.31435/rsglobal_ws/30062024/8174
DOI	https://doi.org/10.31435/rsglobal_ws/30062024/8174
RECEIVED	21 April 2024
ACCEPTED	15 June 2024
PUBLISHED	18 June 2024
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CLEANING WATER SURFACE CONTAMINATED WITH LIGHT OIL FRACTION USING A NEW HYBRID SORBENT

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DOI: https://doi.org/10.31435/rsglobal_ws/30062024/8174

ARTICLE INFO

Received: 21 April 2024
Accepted: 15 June 2024
Published: 18 June 2024

KEYWORDS

Oil Products, Natural Sorbents, Modification, Porous Material, Hydrophobization.

ABSTRACT

For obtaining of porous materials natural sorbents – perlite, zeolite and diatomite were chosen. Thermal and chemical modification and then hydrophobization of the sorbents was carried out. The optimal conditions were determined; amidoaldehyde oligomers were synthesized with the aim of their usage as a matrix in composition of porous materials characterized with high sorption activity and ability to float on the surface of water together with the absorbed compounds. Their removal from the water surface is possible mechanically. Hybrid porous polymers are characterized by selectivity, fire resistance, wide range variability of properties depending on the structure and ratio of initial substances.

Citation: Molodinashvili Zaza, Kopaleishvili Maka, Gabunia Tinatin, Shatakishvili Tamar, Chikaidze Marina, Razmadze Dali. (2024) Cleaning Water Surface Contaminated With Light Oil Fraction Using a New Hybrid Sorbent. *World Science*. 2(84). doi: 10.31435/rsglobal_ws/30062024/8174

1. INTRODUCTION.

The emergence of the oil industry gave a great push to the development of various industrial sectors. Over 2.5 billion tons of crude oil is produced annually in the world. However, the oil industry has negative consequences, namely the pollution of the natural environment by oil and products of its processing. Intensification of oil extraction, evaporation of hydrocarbons during oil refining, loss during production and transportation - all this makes a significant contribution to the worsening of the ecological situation in the world.

As a result of pollution, large areas become unsuitable for agricultural use. The oil entering the soil divides into fractions. At that light fractions of oil gradually evaporate into the atmosphere, and some are mechanically carried out by water into various water reservoirs. Part of the oil undergoes chemical and biological oxidation. A source of pollution is also the wastewaters from petrochemical, oil and gas industries, as well as surface runoffs from the adjacent territories. Accidents that occur at oil-producing, oil-pumping and oil-refining enterprises become a source of catastrophic contamination. As a result, a large amount of carcinogenic compounds enters into the atmosphere, causing many animals and plants to die [1, 2].

In this regard, there is a need to protect the environment from negative components of oil. Disposal of oil wastes is one of the priorities for 2024. Researches in this direction will help in solving problems like rehabilitation of areas exposed to the negative impact of enterprises with oil containing wastes and prevention of the occurrence of accumulation of pollution in the future.

Development of modern and effective methods for removal of oil and oil products from the surface of water and soil currently is very relevant. Therefore, every year more and more methods that can be used to clean the environment from the harmful effects of oil products are being created. At the moment, such methods as mechanical (settling, filtration and centrifugal removal of water pollutants), chemical (chemical ozonation), biological methods as well as methods of physical and-chemical orientation (coagulation and flotation) are known.

Numerous studies showed that the most environmentally friendly, efficient and cost-effective was treatment using sorbents. At the same time, sorbents must have a number of specific indicators: hydrophobicity, the possibility of regeneration, significant adsorption capacity, floatability, chemical and thermal stability. They also should be environmentally friendly and have a low cost [3].

Sorbents according to the method of exposure can be divided into inorganic, organic (natural), organic mineral, synthetic. As inorganic sorbents most often clays and diatomites are used, since they are inexpensive and their production is possible in large volumes. Sand is usually used for sorption of a small area spills. However, according to environmental considerations, the use of sorbents of this type is inefficient since their oil capacity is very low (from 70 to 150%). Moreover, they are unable to retain light oil fractions such as kerosene, gasoline, and diesel fuels. It is impossible and pointless to use them for cleaning of water, since they sink together with oil products. Another reason for the inefficiency of inorganic sorbents is their disposal, which can be carried out by washing them with water containing surfactants and extractants or by burning out. However, progress does not stand still and getting rid of these shortcomings is on its way [1, 5].

Hence the development of new, highly effective sorbent with high sorption ability in respect of petroleum and petroleum products, not sinking in water together with the absorbed compounds, and available owing to the simplicity of production technology and low cost is one of the urgent tasks of the study.

Porous sorbents are also effectively used as heat and sound insulation materials.

According to literary data in polymeric compositions are used both organic (fibrous synthetic polymers: polyesthers and carbocyclic compounds) and mineral (inorganic) raw materials – talc, calcites, basalt fiber, etc. We think it prospective to use perlites, diatomite and zeolite in polymeric compositions.

As polymeric matrix in compositions are used phenol-aldehyde oligomeres, polyurethanes, polyethylene, polystyrene, polypropylene, polyamides, polyacrylates and other class polymers.

We consider amido-aldehyde oligomers as polymers to be used for the intended purpose because of their availability and low cost [4-7].

2. EXPERIMENTAL METHODS AND MATERIALS.

Studies for selection of natural mineral perlites were conducted. Natural sorbents have an advantage in comparison with synthetic sorbents: cheapness, availability. However by effectiveness, purity, homogeneity natural sorbents drop behind synthetic sorbents. From this point of view mineral sorbents – sorbents of silicium series (diatomites), bentonite clays and natural resistant to acids zeolites (perlite, clinoptilolite, etc.) – are of great interest. When choosing natural sorbents their pore sizes for complete sorption of substance, as well as their thermal stability (so that the deformation of the pores does not take place) are to be taken into account. Three main objects were distinguished: natural perlite, diatomite and zeolite [8–10]. On the initial stage natural sorbent – zeolite was chosen which was resistant to aggressive media (acids) and was thermally stable as well, a significant factor from the point of view of exploitation parameters. The optimal conditions for thermal modification of the natural sorbent were determined – heating at 240–700°C during 6 hours.

Researches to determine optimal conditions of chemical modification of the natural zeolite were carried out. Works for obtaining of H-form of the natural zeolite (clinoptilolite) were carried out. The natural zeolite was treated with different concentrations of hydrochloric acid (0,05N; 0,1N; 0,2N; 0,3N) at 25°C.

Chemical modification was carried out to increase the size and activity of the zeolite pores. Optimal conditions (temperature, time, concentration of solutions and ratio of the components) for chemical modification of the zeolite were determined. Several ways of chemical modification were determined, in particular with the help of acids, ammonium chloride (NH_4Cl), potassium chloride (KCl) and other compounds.

Experiments in thermal modification of the diatomite were carried out. Thermal modification of diatomite can be carried out by:

1. Heating at 900–1000°C.
2. Treatment with NaCl and heating at 1000°C.
3. Treatment with SiF_4 and heating at 1000°C.

To determine the optimal temperature of thermal modification the diatomite was heated during 3 hours at 250, 300, 400, 450, 500, 550, 600, 700, 900 and 1000^{0}C.

During heating up to 250°C mainly the absorbed water release takes place. Increasing of the temperature leads to destruction of organic components and widening of pores. At 700°C the size of pores reaches the maximum and capacity of the modified perlite pores increases.

It was determined that introduction of thermally (heating at 700°C) and chemically (by silicium organic compounds) modified perlite into the polymeric composition sharply improves properties of the porous polymere – its density, ability to float, sorption properties, etc.

Natural sorbents – perlite, diatomite and zeolite can be used as remedies for cleaning of polluted with petroleum water. As they are hydrophilic and sink in water it is necessary to carry out their hydrophobization.

Processes of hydrophobization of perlite, diatomite and zeolite were studied.

In particular, hydrophobization both of natural not modified and thermally modified (at 400°C) diatomite was carried out at 250°C during 6 hours in the silicon medium.

The experiment showed that thermally modified diatomite after hydrophobization:

1. Does not get wet in water and does not sink.
2. Effectively absorbs oil from the surface of polluted water.

Diatomite is more prospective sorbent for purification of water-oil emulsions. Heated at 450–700°C diatomite acts more effectively in case of low concentrations of oil ($1.0 \cdot 10^3$ mg/L – $6 \cdot 10^3$ mg/L). If the concentration of oil is high the heating at 1000–1200°C diatomite is used.

To obtain polymeric compositions the complex carbamide-formaldehyde, melamine-formaldehyde and carbamide-melamine-formaldehyde oligomers were synthesized, that are prospective material for usage as matrix in compositions. Synthesis of oligomers was carried out mainly in water solutions, based on amide component and formaldehyde:

The method provides for interaction of amide component (carbamide, melamine) and formaldehyde in water solution in defined reaction media (pH=5–7.5) and temperature (30–100°C) conditions. Correction of the reaction media is carried out by 10% NaOH solution and formic acid. Ratio of the resulted components (amide component: formaldehyde) is 1: 1.7, respectively. Water solution of formaldehyde was used [11-14].

Amide oligomers were obtained by polycondensation in alloy with ratio of the obtained components (carbamide : aldehyde) 1:1.1, respectively, at 100°C, duration of the reaction 1 hour.

The composites were prepared from diatomite (both natural and modified) and amido-aldehyde oligomer (with different percentage) according to the developed by us technology: foaming agent, resorcin and water mixture were placed into the utensil. After their good mixing 2.5 ml of mixture were foamed by air stream to obtain stable foam. A certain amount of amido-aldehyde oligomer was added to the foam with preliminarily introduced certain amount of natural sorbent. Foaming was continued by air stream until full effervescence and obtaining of stable foam.

It was determined, that properties of the obtained porous hybrid polymer were affected by the ratio of amide oligomer to diatomite, and the reaction media. The results gave us possibility to make a conclusion: the optimal mass ratio of diatomite and amido-aldehyde oligomer to obtain effective material is 0.3:0.7, respectively. Increasing of the diatomite amount up to 50% (in relation to the oligomer) the heat stability, density, fire resistance is increased, physical and mechanical properties are improved. But further increase of the ratio results in worsening of the material properties.

The effect of pH on the formation of a hybrid polymer was studied. Its correction makes it possible to obtain materials with the desired properties. The rapid hardening and the final formation of the exploitation properties of the material depend on the pH. It should be noted that the materials obtained on the basis of amido-aldehyde oligomer and diatomite are equal in efficiency to the expensive materials obtained on the basis of polyurethane. At the same time, they are 10-12 times cheaper than polyurethane materials.

Together with carbamide-formaldehyde and melamine-formaldehyde homogeneous polymers the complex carbamide-hyaline-formaldehyde polymers were obtained.

At the first stage of polymer formation in aqueous solution, methylol derivatives of melamine were obtained, and then they were converted to oligomers by heat treatment (100°C) and lowering the pH to 5-6. By interaction of the obtained oligomers and a foaming agent (foaming agent, 60% H_3PO_4, resorcin and H_2O) a foam-polymer was obtained, from which polymers with a porous structure were prepared.

3. RESULTS AND DISCUSSION.

To study the sorption properties of the polymer the water artificially polluted with petroleum product (benzene) was taken. Porous polymers (sorbents) were placed into the resulting emulsion for a defined time (1, 3, 5, 7, 10 days). The sorbents were hybrid materials derived from carbamide-formaldehyde oligomers and modified diatomite. After then, the extraction of porous samples (sorbents) from the aqueous medium was performed. Using the spectral analysis, the concentration of the petroleum product remaining in the aqueous emulsion was determined.

The study showed that porous composites are characterized by much higher sorption properties than natural and modified diatomite. Thermally modified, hydrophobized diatomite almost completely absorbs petroleum product if its concentration does not exceed $6 \cdot 10^3$ mg/L, and at higher concentration - $14 \cdot 10^3$ mg/L, the amount of petroleum product absorbed by diatomite decreases. Under these conditions high sorption properties are shown by hybrid composites obtained on the basis of the amido-aldehyde oligomer and containing 30% of natural or modified diatomite. Studies of the properties of sorbents were carried out using the spectral and chromatographic methods.

Samples of porous polymer with different percentages of diatomite - 20, 25, 30 and 40% were obtained. The best option was the 25% content of diatomite. The resulting polymer has a high strength and increased porosity. Obtaining of polymer occurred in a shorter time than in other cases.

The influence of various factors (reaction medium, oligomer concentration, air flow intensity, mixing frequency, amount of natural sorbent, etc.) on the formation of a hybrid porous polymer was studied. It was established that the optimal conditions for polymer formation were the following: pH of the reaction mixture <7, oligomer concentration - 55%, intensive air flow, maximum mixing frequency, temperature 20 ± 5°C and content of natural sorbent - 25%.

The obtained samples of mixed polymer containing different percentage of diatomite were tested for sorption capacity, the results of which are shown in the table below. It has been established that for improvement of sorption properties of a polymer, both thermal and chemical modification of diatomite is of great importance.

The study showed that if the concentration of petroleum products in the polluted water is $6{\cdot}10^3$ mg/L, then a sample of mixed porous polymer containing 25% thermally and chemically modified diatomite completely absorbs petroleum products from the surface of the water in five days. In case of polymer sample containing only thermally (1000 °C) modified diatomite the sorption capacity is well manifested at a low concentration of contamination with petroleum products $1{\cdot}10^3$ mg/L – 6 10^3 mg/L. Work continues.

Table 1. The results of sorption by hybrid porous sorbent from the surface of water polluted with benzene (light fraction of petroleum).

	Samples of porous hybrid materials[x]	Sample weight, g		Amount of absorbed benzene[2x]	
		Before sorption	After sorption	g	%
1	Carbamide-formaldehyde polymer	3.24	5.42	2.18	67
2	Hybrid porous polymer (carbamide-formaldehyde oligomer – 70%, natural diatomite – 30%)	3.53	6.32	2.79	79
3	Hybrid porous polymer (carbamide-formaldehyde oligomer – 70%, modified diatomite – 30%)[3x]	4.28	7.85	3.57	83
4	Hybrid porous polymer (carbamide-formaldehyde oligomer – 60%, modified diatomite – 40%)	5.15	8.67	3.53	68

[x] – Size of the sample 3x2x1 cm^3, ρ=0,2-0,7g/cm^3.

[2x] – Time of sample contact with benzene – 5 hours (in water-benzene emulsion); amount of benzene -5ml.

(d=0.879g/cm^3, $t_{boiling}$= 80^0C). Water – 100 ml.

[3x] – Diatomite is thermally modified (900°C) and hydrophobized with polymethylphenylsiloxane.

4. CONCLUSION.

1. Natural sorbents – perlite, diatomite and zeolite – were chosen.
2. For the purpose of activation of sorbents they were thermally and chemically activated.
3. Optimal conditions of thermal modification of natural sorbents were determined: for diatomite – heating at 1000°C for 3 hours; for zeolite – heating at 240–700°C for 6 hours; and for perlite – heating at 400–600°C for 3 hours.
4. Chemical modification of zeolite was carried out by 0.1N ammonium chloride; of diatomite – by treatment with SiF_4; of perlite – by silicium organic compounds.
5. Hydrophobization processes of diatomite, perlite and zeolite were studied. In particular, hydrophobization of natural unmodified and thermally (400°C) modified diatomite was carried out at 250°C for 6 hours in silicon area.
6. Amide oligomers were synthesized (amide component:formaldehyde). Ratio – 1:1.8, respectively. Water solution of formaldehyde was used.
7. Amide oligomers were as well obtained by polycondensation in melt with molar ratio of initial components (carbamide:aldehyde) 1:1.2, respectively, at 100°C, duration of the reaction – 1 hour.
8. Optimal mass ratio of diatomite and amido-aldehyde oligomer was determined – 0.3:0.7, respectively.
9. Influence of different factors on the process of hybrid porous polymer formation was studied.
10. The obtained samples of mixed polymer with different percentage of diatomite were examined for sorption ability and the study showed that porous composites were characterized by much higher sorption properties then polymer alone or natural and modified diatomite alone.

REFERENCES

1. Peters A. Oil spills and the environment // Ecology. 2006, # 4, 11 p.
2. Gridin O.M. About oil sorbents // Metallurgist. 2000, # 10, pp. 25–31.
3. Zheltov, M. Sorbents in the fight against oil spills // Aquaterm. 2012, # 1 (65). pp. 98–101.
4. Toroptseva A.M., Belogorodskaya K.V., Bondarenko V.M. Laboratory Workshop in Chemistry and Technology of High-Molecular Compounds". Leningrad, "Chimia'', 1972, p. 218.
5. Gladun V.D. Inorganic adsorbents from industrial wastes for treatment of industrial wastewaters / V.D. Gladun, N.N. Andreeva, L.V. Akatieva, O.G. Dragina // Ecology and Industry of Russia. 2000, # 5, pp. 17–20.
6. Abbasov V.M. Ecological problems of the Caspian Sea associated with the extraction and processing of oil. Theses of the V Baku International conference, September 3-6, 2002.
7. Dvadnenko M.V., Privalova N.M., Lyavina E.B., Protsai A.A., Dinchenko Yu.V. The use of sorption technology for the treatment of oil-containing wastewaters // Fundamental researches. 2009, # 55. pp. 45–46.
8. Patent 2587440 of the Russian Federation. Composition for obtaining of sorbent based on carbamide-formaldehyde resin // Melkozerov V.M., Vasilyev S.I., Lapushova L.A.; publ. 2016. Bull. No. 17.
9. Patent 2593160 of the Russian Federation. Polymer composition for plastic foam // Melkozerov V.M., Vasilyev S.I., Ortman A.S; publ. 2016. Bull. No. 21.
10. Lapushova L. A., Vasiliev S. I. Results of the study of the structure of the polymer sorbents "Uni-Polimer-M" for liquidation of anthropogenic spillage of oil and oil products // Protection of the environment in the Oil and Gas Complex. 2015. No. 6. pp. 17-21.
11. Vasilyev S.I., Lapushova L.A., Melkozerov V.M., Matveykina Ya.V., Gorbunova L.N. Results of the study of hydrophilia of polymer sorbents from the "Unipolymer" series // Systems. Methods .Technologies. 2016. № 1 (29), pp. 135-139.
12. Melkozerov V.M., Vasilyev S.I., Velp A.Ya., Krylyshkin R.N., Maryanchik D.I. Operational properties of polymeric sorbents // J. of Sib. Federal Univ. Engineering & Technologies. 2011. No. 4, pp. 369-379.
13. Levchenko A.G., Vitkovsky M.I., Kurkin V.A., Fedotova A.S. Recultivation of agricultural soils using the "Unipolymer-M" sorbent // Protection of the environment in the Oil and Gas Complex. 2013, No. 10, pp. 42-54.
14. Bazunova M. V., Idrisov I. F., Bazunov A. A., Akhmetkhanov R. M. Sorption-active hybrid polymer nanocomposites based on polyethylene and inorganic components // Scientific. almanac, 2017, No. 2-3 (28), pp. 422-426.