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PREPARATION AND APPLICATION OF A MAGNETIC COMPOSITE SORBENT FOR COLLECTING OIL FROM A WATER SURFACE

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ABSTRACT

A oil products are among the most dangerous pollution of water objects. They have a deleterious effect on the physiological and biochemical processes in the body of biological objects. In recent years, more and more attention is paid using of industrial waste for water treatment from oil products. In this study, the composite magnetic sorption material was received by chemical sedimentation using of the waste of MDF production (wood fiber) and iron chloride (II) and (III). Fractional composition and physico-chemical characteristics (Tamped density, content of moisture, ash content, buoyancy, specific surface area) of the reagent was detected, the micrographs were obtained by scanning electron microscope. The elemental composition of materials was identified using the method of energy-dispersive X-ray spectroscopy. The remanent magnetism and the coercive force of the samples of modified wood fiber were calculated According of obtained hysteresis loops. IR spectra of the sorption materials were obtained and described using the method of FTIR spectroscopy in a frequency range of 400–4000 cm^{-1}. Oil sorption capacity and water uptake of waste wood fiber and magnetic composite sorbent were evaluated in static system. Increase of oil sorption capacity and decrease of water uptake after modification of waste wood fiber was observed. Experiments to remove oil pollution from the water surface were carried out. The effectiveness of the proposed sorption material was discussed.

Keywords: oil, waste, wood fibers, magnetite, sorption material.

INTRODUCTION

The most effective method purification of water objects from spills of oil and oil products is the sorption purification, where as sorption materials (SM) used materials of natural and artificial origin, having a high sorption capacity. For liquidation of spills of oil produce and use many different SM, which are divided into inorganic, organic, organo- mineral and synthetic [1]. However, a limiting factor in the use of SM for the liquidation of oil spills is their relatively high cost. In this regard, especially nowadays, the finding a highly effective and inexpensive sorbents of oil and products of its processing is urgent task. The particular interest is alternative materials made from waste industrial and agricultural production [2].

SM must correspond to a number of requirements that apply to the oil sorbents: accessibility, low cost, possibility of recycling, and no secondary pollution. Of particular interest are SM based on cellulose. The advantages of such SM in comparison with synthetic materials are the presence of various functional groups and physico-chemical characteristics of the polymer matrix. As such materials can be used waste of timber industry: leaves, sawdust, tree bark [3-5].

The effective sorbents of oil are synthetic fibrous materials. They are easily and quickly placed on the oil spills and pick up after the last impregnation, and characterized the ability to re-use after extraction of oil [6]. The composite materials are widely used as fibrous sorbents, the preparations of which use a variety of plant waste as the filler. It is known that in such materials are able to combine a significant degree of substitution of the synthetic material (up to 45 % and above) and high rates of oil capacity. In addition, the availability and cheapness of plant fillers can significantly reduce the cost of synthetic composites that stimulate their wide application for the solution of environmental problems [7]. However, a significant disadvantage of SM of plant origin is high rates of water uptake, which reduces the efficiency of their use for oil gathering. For eliminating such disadvantage use various methods of modification.

The aim of this work was to obtain magnetic composite sorbent (MCS) based on waste wood fiber (WWF) production of MDF and magnetite (Fe_3O_4), the study of its physico-chemical characteristics and adsorption properties with respect to petroleum products. The advantage of this material compared to non-magnetic is that at contact the surface cleaning water from oil products, significantly simplifies the collection of waste material when exposed magnetic forces. In the course of work using the methods of electron microscopy, x-ray analysis and IR-spectroscopy we evaluated the effect of modification on physico-chemical properties of WWF. For assessing sorption properties the experiments were conducted to determine the water uptake of original and modified fibers, oil sorption capacityin relation to oil of the Devonian deposits, as well as experiments were performed on modeling the removal of oil layer from the water surface. The efficacy of the proposed SM was discussed.

METHODS

As a starting material to obtain the SM applied the WWF to the production of MDF, formed on the timber industry. The MDF boards on the production are made mainly of wood of soft deciduous species (aspen, birch, linden). WWF is formed at the stage of formation of fibers in the technological cycle of production of MDF and it is

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defect, unfit for further use in production [4]. For experiments the averaged sample was selected from all areas for the temporary storage of waste.

For getting SM The settlement of nanoparticles Fe_3O_4 produced in the next weight ratios of components: $WWF:FeCl_3:FeCl_2 = 10:2.25:1$ on the surface of WWF in the aquatic medium under the influence of ultrasonic vibrations with a frequency of 35 kHz at a temperature of 80±1 °C when one and a half the excess of ammonium hydroxide. The resulting product was repeatedly washed with water until neutral environment. To reduce degree water uptake and increase the hydrophobic nature of the material treatment were produced using hydrophobisator "Akvasil" the rate of 0.5 dm^3 per 1 kg, and then were subjected to drying at a temperature of 110 ° C for 8 hours. Determination of fractional composition of SM was carried out using the sieve sieving method on a particle size analyzer A-30 with a set of sieves normal accuracy with the cell size 5; 3; 2; 1 and 0.5 mm. To determine tamped density, hygroscopic moisture content and ash content using standard methods [5].

The buoyancy of the SM was determined by the method of [8], for which the sample SM weighing 3 g was placed in a beaker with volume of 0.5 dm^3, half-filled with water. The contact time of the sorbent with water was 72 hours. After a given time to stay afloat SM was removed and subjected to drying in a drying cupboard at a temperature of 103°C until constant weight. The number of drowning SM was calculated by the use weight difference.

The change in the structure of wood fibres was recorded by scanning electron microscopy with a tungsten electron source. For elemental microanalysis was used energy dispersive x-ray spectrometer brand "the JSM–6000". To measure the specific surface area used in the analysis of cryoadsorption vapor of high purity nitrogen at -195 °C BET Surface Area Analyzer "Quantachrome Nova 1000e"
Magnetic measurements were performed on an automated complex [9]. A limit of the static hysteresis loops was carried out for determining the values of saturation magnetization and coercive force. In this dimension on the Helmholtz coils was applied a sinusoidal voltage with a period of 90 s and a voltage of 100 V. the Induction recorded by the Hall sensor and the test sample was placed in the coil of the induction sensor in the region of greatest field homogeneity [10].

Infrared spectra were shot on FTIR spectrometer brand "Avatar 360" in the frequency range 400-4000 cm^{-1}. Samples for shooting IR spectrometer the test samples were made in the form of tablets [11].

For determining the maximum values of the oil sorption capacity SM in static conditions a metal grid were placed in Petri dishes, 0,05 dm^3 of oil were poured and the sample SM weight of 1g was applied continuous layer. As the sorbate medium sour oil of Devonian deposits used. After 30 minutes the samples were removed and after draining the excess amount of oil was weighed in the balance. The value of oil sorption capacity was calculated

as the ratio of the weight of oil uptake to the weight of the SM:

$$A = \frac{m_1}{m_0},$$

m_1 - the weight of oil uptake, g; m_0 – weight of SM, g [12].

SM water uptake was determined according to the method similar to the definition of oil sorption capacity.

In experiments to establish the dependence of oil uptake from contact time SM Petri dishes poured with 0.05 dm^3 of distilled water and 0.005 dm^3 of oil. After the surface of formed oil layer was applied 1 g of the sample in SM. After defined time periods (from 15 min to 5 hours) SM were removed and weighed. The weight content of remaining in the Petri dish of oil was determined by extracting the last CCl_4 and then the amount of oil uptake was calculated by the use difference of the weight.

Experiments on the simulation conditions of oil spills was prepared in a similar manner, samples of SM were removed after 30 minutes and in addition to oil uptake on the weight difference calculated number sorbed water.

To create an oil layer of a certain thickness under laboratory conditions in a Petri dish poured with 0.05 dm^3 of distilled water on the surface of which drops made of oil and as the formation oil slick measured its thickness [13]. After that, the surface of formed oil layer was applied 1 g SM. The value of the oil and the water uptake was determined similarly to the experiments on the simulation conditions of the oil spill.

RESULTS

In the initial phase of the study the physico-chemical characteristics of original and modified SM were examined. Figure-1 presents the results of the fractional analysis of the MCS.
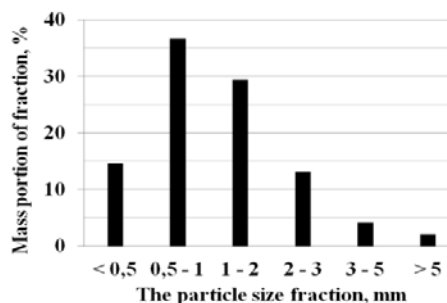

Figure-1. Fractional composition of MCS.

Table-1 shows the results of determination of tamped density, hygroscopic moisture content, ash content, buoyancy and specific surface area of materials studied.

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Table-1. Physico-chemical characteristics of SM.

Sample	Tamped density, g/cm³	Moisture content %	Ash-content, %	Buoyancy, %	Specific surface area, m²/g
WWF	0.148	14.5	0.46	74.6	112
MCS	0.169	3.52	5.84	98.9	161

In the course of work resulting surface micrograph and Infrared spectra of original and modified fibers (Figures 2, 3), by energy dispersive x-ray spectroscopy determined the elemental composition of the samples (Table-2).
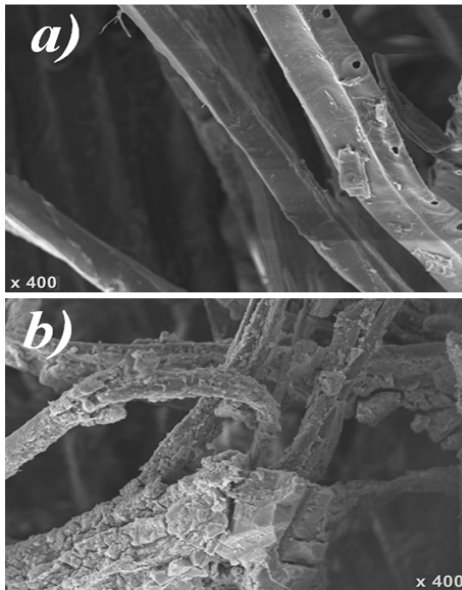
Figure-2. Microphotography WWF (a) and MCS (b).
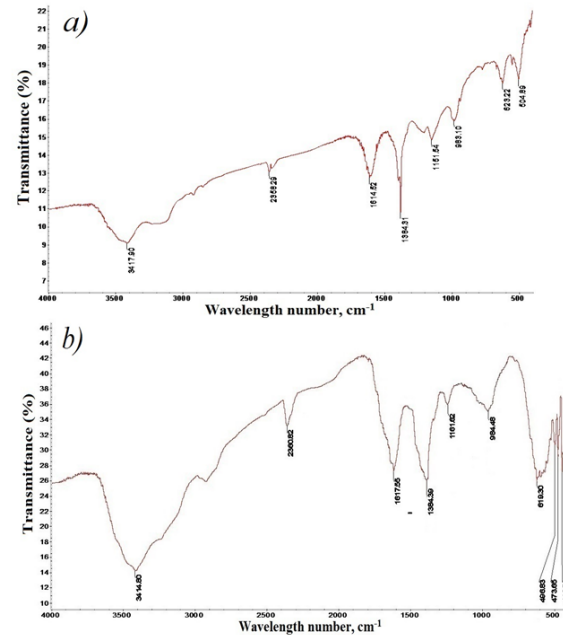
Figure-3. Infrared spectra WWF (a) and MCS (b).

Table-2. Elemental composition of SM.

Sample	Weight percent , %							
	O	C	N	Ca	Mg	Si	Na	Fe
WWF	39.1	35.7	24.5	0.26	0.25	0.04	-	0.15
MCS	38.5	33.4	22.3	0.19	0.18	0.08	0.03	5.32

According to the obtained hysteresis curve (Figure-4) calculated saturation magnetization and coercive force of samples of the modified fiber (Table-3), for comparison the Table-also shows the magnetic properties of similar materials.
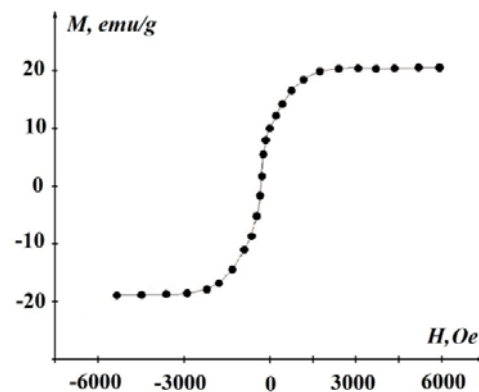
Figure-4. Hysteresis curve MCS.

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Table-3. Magnetic characteristics of SM.

Sample	Saturation magnetization, *emu/g*	Coercive force, *Oe*	Folios
MCS	18.0	12.0	-
MN202-IIm	14.9	16.3	[14]
A novel magnetic resin Q100	4.7	-	[15]
Magnetic powder resin Q150	9.7	8.2	[16]
Fe_3O_4-HA20-C	65	15.0	[17]
Synthetic Fe_3O_4	82	200	[10]

In a static conditions the values of maximum oil sorption capacity, water uptake, and the degree of extraction of oil (Table-4), for comparison the Table-also presents the characteristics of various materials are used to collect oil.

Table-4. The maximum values of oil sorption capacity and the water uptake.

Sample	Oil sorption capacity, g/g	Water uptake, g/g	Degree of extraction of oil, %	Folios
WWF	9.23	9.51	82	-
MCS	10.25	2.34	84	-
Sawdust	1.7	4.3	10-20	[18]
Fiberglass	5.4	1.7	60	
Power-sorb	13-25	3-6	70-80	
Irvelen	12-25	5-8	75	

The Figure-5a shows the characteristic curve of oil uptake from time of contact with the SM, the Figure-5b - a characteristic curve of oil and water uptake from the thickness of oil layer.
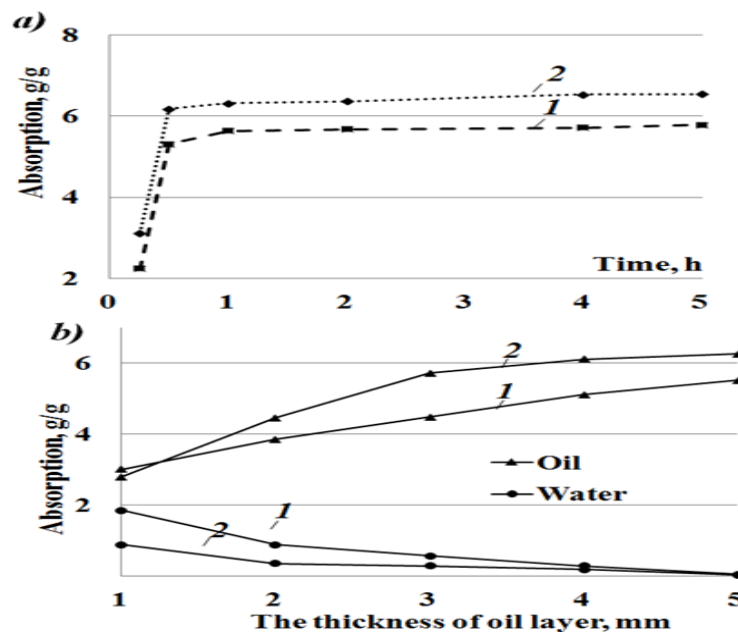

Figure-5. a) The characteristic curve of oil uptake from contact time; b) The characteristic curve of oil and water uptake from thickness of oil layer (1 - WWF, 2 - MCS).

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The Table-5 shows the results of experiments on the simulation of the removal of oil layers from the water surface with the use of WWF and the MCS.

Table-5. The value of the oil and the water uptake WWF and MCS.

Sample	Oil uptake, g/g	Water uptake, g/g	Aggregate value of the oil and the water uptake, g/g	Removal rate of the oil, %
WWF	5.68	0.73	6.41	96.32
MCS	6.35	0.24	6.59	99.78

DISCUSSIONS

In the study, physico-chemical characteristics of WWF and MCS were examined. According to fractional analysis and the obtained micrograph, the fiber is a system of randomly packed, freely distributed in the space of the filaments with the predominant size of 0.5-3 mm. The original fiber has a high enough value of the indicator of buoyancy. Low ash content (0.46 %) indicates a high content of organic matter; it's a fairly important condition for the utilization of spent sorbent by burning. We can see the significant increase degree of buoyancy after modification of waste wood fiber; it's associated with application of hydrophobisator, as well as increases the ash content to 5.84 %, due to the presence of iron. The roughness and porosity of the surface is an important parameter affecting the amount of oil sorption capacity SM except water uptake. According to the source micrograph the original fiber has many internal pores, allowing the oil to contact with more surface per unit time, and the use of the modification allowed to increase the roughness of surface while maintaining the porosity of the material. This increase of roughness and, consequently, surface area SM enhances the sorption capacity [19].

According to elemental analysis (Table-2) the main components of both the original and the modified fibers are oxygen, carbon and nitrogen. The presence of small amounts of calcium, magnesium, silicon and iron in the structure of the original fiber is due to the use of bleaching and bonding components in the manufacture and adhering of mechanical particles. After modification there is a noticeable increase in the mass fraction of iron associated with magnetite deposition on the fiber, as well as a small increase in the mass fraction of silicon and sodium due to the application of hydrophobisator.

In the presented IR spectra of the original fiber The absorption bands are observed due to the stretching vibrations of hydroxyl groups in the region 3500-3400 cm^{-1}, nitrile groups in the region 2360-2350 cm^{-1}, carbonyl group in the area 1620-1610 cm^{-1} and carboxyl groups in the area 1390-1380 cm^{-1}. After deposition of magnetite in these areas, we can see an increase of transmission factor associated with the flow of the hydrolysis of cellulose and lignin as a result of the modification (Denisova *et al.* 2016) and the expansion peaks associated with the increase in the number of hydrogen bonds. In the shortwave part of the spectrum, both the original and modified fibers stretching vibrations of carbohydrate and alcoholic hydroxyl groups are observed in the region 1150-950 cm^{-1}, the deformational C-C (skeletal) vibrations are characteristic for cellulose in the area of 620 cm^{-1} [20]. A lot of intense bands are produced in the range 500-450 cm^{-1} related to the characteristic vibrations of Fe-O of magnetite as a result of modifications [21].

Determination of the magnetic characteristics of the obtained composite material was the next stage of research. The measurements showed that the SM has magnetic properties. The magnetic hysteresis loop isn't on the magnetization curve (Figure-4), it's an indicator of the presence of nanosized magnetic particles [22]. According to the data obtained, the saturation magnetization of the modified SM is 19 emu/g, the coercive force is 12 Oe, it's higher than some well-known sorbents [14-16]. It should also be noted that for the removal of contaminated sorbents using the method magnetic separation is sufficient the value of the specific magnetization of the order of ten emu/g [23].

In static conditions the maximum value of the oil sorption capacity is determined in relation to the Devonian oil WWF; it's made up 9.23 g/g. After modification the increase of oil sorption capacity is observed associated with an increase in the specific surface area of the material as result the deposition of magnetite on the fiber, as well as a significant decrease of oil uptake due to exposure to hydrophobisator.

The studies the optimal contact time required to remove oil layer with a thickness of 3 mm was determined. The time of sorption equilibrium for both the original and the modified SM was determined and is 30 min. After it a substantial increase in the sorption capacity doesn't occur (Figure-5a).

Figure-5b shows the effect of oil layer thickness on the oil and water uptake for WWF and the MKS. The amount of water uptake by the absorbents along with the oil decreases with increasing the oil layer thickness, the water uptake is less than 0.05 g/g with the thickness of the oil layer of 5 mm.

Table-5 presents the results of experiments on the simulation of the removal of oil layer from the water surface with the use of WWF and the MKS. As can be seen from the obtained results, both the original and the modified SM have high enough values oil uptake and aren't inferior to industrial sorbents Power-sorb and Irvelen representing net polymer fiber. The total value of the oil and water uptake for the modified SM made up 6.59 g/g, the degree of removal of oil - 99.78%.

Thus, the research results of physical-chemical and sorption properties of SM presented in this work show that the proposed method of modification of the waste

wood allows to obtain a magnetic composite material with a high index of oil sorption capacity that makes possible the use of the proposed sorbent for liquidation of oil spills from the water surface.

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