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SORBENTS BASED ON BIOPOLYMERS OF DIFFERENT ORIGIN CONTAINING MAGNETITE FOR REMOVAL OF OIL PRODUCTS AND TOXIC IONS FROM WATER

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Oil and oil products enters surface waters as a result of man-made disasters, caused, in particular, by military operations. In order to prevent ecological catastrophe, it is necessary to remove hydrocarbons from water surface. The paper is devoted to the development of materials for the extraction of non-polar liquids from aqueous media. Magnetic sorbents based on non-carbonized biopolymers (both plant cellulose and keratin) are proposed. Biopolymer matrices of different morphology on the level of fiber bundles were used for the composite preparation. Dependent on origin, the matrices are characterized by different morphologies at the level of fiber bundles: they are straight (cellulose obtained from wood and corn cobs), helical (cellulose of tea leaves or scaly (keratin from animal wool)). Magnetite particles were inserted into biopolymer matrices after the removal of non-cellulose and non-keratin inclusions from them. The samples were investigated with SEM and FTIR techniques, magnetite was identified with XRD analysis. The most homogeneous distribution of magnetic particles, a size of which is less than 1 μm , was found for the matrix obtained from corn cobs. This composite contained the least amount of iron (0.24 mass. %), namely this sample demonstrates the best flotation. The sorbent based on cellulose from tea leaves contained 71% of iron: the particles sink almost completely. The capacity towards non-polar liquids was estimated as follows (g g^{-1}): 1.6–8.6 (vegetable oil), 10.5–16.4 (crude oil), 9.8–14.5 (kerosene). After the removal of crude oil from water surface, no film of this liquid was visually observed. The value of chemical oxygen demand was $\approx 0.2 \text{ mgO}_2 \text{ dm}^{-3}$, this is less than the demand for drinking water. Moreover, the sorbent can be easily removed from water surface with magnet. As found, the sorbents can be used for removal of toxic metal ions from water. As found, magnetic particles improve sorption of Pb^{2+} ions but decrease Cd^{2+} sorption. Thus, the sorbents with small content of inorganic modifier can be used for the removal of oil and oil products from water surface. The sorbents, which demonstrate bad flotation, can be used for the recovery of inorganic ions. The advantages of biopolymer-based sorbents over known material is a simple preparation procedure that involves cheap and available feedstock. Moreover, the sorbents can be easily separated from aqueous phase with magnet.

Keywords: Biopolymers, magnetite, magnetic composite, crude oil, oil products, water purification

INTRODUCTION

One of the cheapest ways of delivering oil and oil products to consumers is water transport. However, the transportation of this raw material in this way is associated with the risk of its spillage: first of all, the areas of sea and ocean deposits as well as ports are dangerous areas. Moreover, the risks are significant during oil production from water deposits [1]. In recent years, there have been a number of cases of spills of oil and oil products over the world. Now this problem is very important for Ukraine due to military operations. After the explosion of Deepwater Horizon oil rig in 2010 (Gulf of Mexico), oil spill disposal and related

environmental remediation techniques have attracted considerable attention [2–4]. It is necessary not only to prevent possible contamination of water with liquid hydrocarbons, but also to use environmentally friendly technologies to clean the water surface from these pollutants.

The most effective methods for cleaning water surfaces is extraction with sorbents [5]. However, known sorbents have such disadvantages as low absorption capacity, high cost and insufficient flotation. For “ideal” adsorbent materials, such properties as hydrophobicity, oleophilicity, high capacity, low density, environmental friendliness should be

inherent [6]. Ease of manufacture and low cost are also of key importance. Thermally expanded graphite [7, 8], carbon aerogels [9, 10], graphene [11] are attractive for this purpose, however, the preparation of these materials requires significant energetic expenditures. The most suitable are cheap and available agricultural waste.

The natural materials, which have not been treated with chemical reagents, were considered, for instance, a mixture of straw and peat [12, 13]. The function of plant additives, in particular, is to prevent the dispersion of peat in aqueous media. The mixture was used for the removal of crude oil and diesel fuel from water: the capacity values of $6.3\text{--}9.4\text{ g}\cdot\text{g}^{-1}$ have been reported. In order to increase sorption capacity of plant feedstock, chemical treatment is used: acetylation of hydroxyl groups of cellulose fibers has been performed [14]. This approach allowed one to achieve sorption capacity of $42.5\text{--}52.6\text{ g}\cdot\text{g}^{-1}$ towards oil products.

Other method is obtaining polymer and polymer-inorganic composites based on plant cellulose. Cotton and cane cellulose was applied to preparation of composites with a mixture of polypropylene and polyethylene fibers [15]. The capacity was $11\text{--}14\text{ g}\cdot\text{g}^{-1}$ towards engine oil. A common technique is the insertion of silica or ZnO into cellulose fibers followed by hydrophobization of the surface of inorganic oxides [16–23]. Such modifier as reduced graphene oxide has been proposed [24–26]. Though the obtained sorbents are hydrophobic, their preparation procedures are rather complex. Moreover, the problem of the removal of solids from water surface appears.

The easiest way to solve this problem is insertion of magnetic particles into cellulose fibers. Magnetic sorbents, which are used for different purposes, are known [27–29]. For example, composite sorbent based on corn straw containing magnetite has been obtained [30]. Cellulose was previously functionalized with aminogroups. The sorbent is capable to sorb phosphate and chromate anions from water. The maximum sorption capacity for phosphate ions is $40\text{ mg}\cdot\text{g}^{-1}$ at $25\text{ }^{\circ}\text{C}$, it is $285\text{ mg}\cdot\text{g}^{-1}$ for chromate anions. Regarding non-functionalized cellulose [31–33], its capacity towards inorganic ions is much lower comparing with synthetic polymers, especially ion exchange resins modified with inorganic constituents [34–36]. In the last case,

the enhancement of sorption properties of the polymer is due to specific interaction of ions with functional groups of inorganic modifier like zirconium hydrophosphate [37] or strongly charged surface of multivalent metal oxides [38–40].

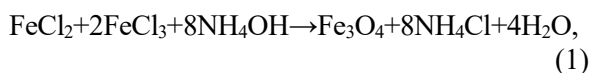
Thus, it is possible to suppose that modifying biopolymers with magnetic should provide easy separation of sorbents saturated with oil products from water. On the other hand, the modifier can affect sorption of inorganic ions. The aim of the investigation is to clarify the effect of the origin of biopolymer matrix on sorption properties of the composites containing magnetic modifier. The tasks involve synthesis of magnetic particles in different biopolymers, research of their composition and morphology, and also testing sorption properties towards oil products as well as toxic inorganic ions like Pb^{2+} and Cd^{2+} .

EXPERIMENTAL

In order to obtain low cost sorbents, a number of materials of plant and animal origin were used: cobs of corn (*Zea mays*), leaves of tea (*Camellia sinensis* L. Kuntze), shavings of wood of white poplar (*Populus alba*), wool of a dog of the German Shepherd breed (Deutscher Schäferhund). The samples were marked as CC (cellulose obtained from corn cobs), TL (tea leaves), PW (poplar wood), DW (dog wool).

The raw material was crushed, washed with deionized water, dried at $95\text{--}97\text{ }^{\circ}\text{C}$ down to a constant mass, kept for a day in a $10\text{--}12\%$ NaOH solution. The aging procedure in the alkaline solution was repeated several times until the non-cellulose and non-keratin inclusions were completely removed. The removal completeness was evidenced by the absence of color of the alkaline solution. After that, the samples were successively washed with deionized water, 0.1 M HCl solution, and again with water until the effluent was neutral. Then the samples were dried at the temperature indicated above. The samples were marked as CC-0 etc.

Before the synthesis of magnetic sorbents, the samples of biopolymers were boiled in deionized water to remove air from pores. Then the samples were impregnated with a mixed solution of FeCl_2 (0.1 M) and FeCl_3 (0.2 M), a NH_4OH solution (10 M) was gradually added dropwise up to pH 11 under agitation [41]. Following reaction occurred:



magnetite particles were formed by this manner inside and outside the biopolymer matrix. Then the composites were washed with deionized water down to pH 7, dried under ambient conditions and at 120 °C. The powder of magnetite, which was not precipitated in the biopolymer pores, was collected for further investigations. The samples were marked as CC-Fe and so on.

In order to perform SEM observation and chemical analysis, a SEO-SEM Inspect S50-B microscope was used. Preliminarily the samples were coated with ultrathin Ag film. FTIR spectra were obtained using a Spectrum BX FT-IR spectrometer (PerkinElmer Instruments, USA), the samples were preliminarily grinded up and compressed with KBr. XRD investigations were performed using a DRON-3 spectrometer (Burevestnik, RF) supplied by Cu anode and Ni filter.

In order to estimate flotation, the weighted sample of composites were inserted into vessels filled with water. After intensive agitation during 15 min, the sorbent was removed from the water surface. A part of the sorbent sank to the bottom, the solid and liquid were separated. The portions of the sorbent from the water surface and vessel bottom were dried at 120 °C and weighted. The sorbent from the bottom was used further for sorption of inorganic ions.

The capacity towards crude oil and kerosene were determined according to the weight increase before and after sorption. Sunflower oil was also used for comparison. The wetting angle was determined based on drop photos obtained with a Nikon d3100 digital camera. Crude oil was also removed from water surface, initially the mixture of 100 cm³ of water and 1 cm³ of oil was shaken during 15 min. Then 0.1 g of sorbent was added, the mixture was shaken again during 15 min. The sorbent was removed from water surface with magnet. Chemical oxygen demand was determined in liquid phase before and after oil sorption [42].

Sorption of Pb²⁺ and Cd²⁺ ions from one-component solutions was also investigated. Their initial concentration was within the interval of 0.0001–0.01 mol·dm⁻³. The sorbent mass was 0.1 g, the solution volume was 0.02 dm⁻³, the time of contact of liquid-solid was 24 h. The

sorbent was separated from the solution, washed with deionized water and treated with a 0.1 M HCl (0.02 dm⁻³). The effluent was analyzed with a S9 Pye Unicam atomic absorption spectrophotometer (Philips, the Netherlands) at 217 (Pb) and 228.8 (Cd) nm.

RESULTS AND DISCUSSION

Electronic spectra of unmodified CC biopolymer (Fig. 1 *a*) predictably shows a dominance of carbon and oxygen (in fact, oxygen and hydrogen). A presence of Ag is due to ultrathin conducting film on the sample surface, copper can be partially caused by the substrate, where the sample was fixed. However, a number of microelements is present in the samples. Chemical composition of biopolymers is shown in Table 1. It should be stressed that keratin (DW sample) contains considerable amount of nitrogen, this is typically for proteins. At the same time, no nitrogen has been found for cellulose-based samples. Note that atypical elements were recorded for all samples (Al), and for cellulose obtained from tea leaves and wood (W). It indicates the ability of plants and woods to accumulate metals, when the ecology situation is not satisfied. A presence of tungsten in agriculture product (TL sample) is especially alarming.

Regarding modified biopolymers, the peak, which is attributed to Fe, becomes more expressed (Fig. 1 *b*) indicating increase of iron content.

The SEM method gives a possibility to recognize the structure of biopolymers on the level of fiber bundles. In the case of CC-0 sample, the bundles are straight, they branch out and intertwine with each other (Fig. 2 *a*). Their thickness is several microns, the particles of residual non-cellulose inclusions are visible on their surface. Modifying causes formation of cracked film on the bundle surface (Fig. 2 *b*). The origin of this film can be inorganic (due to Fe₃O₄ precipitation), organic (transformation of residual non-cellulose inclusions in ammonia solution and thermal treatment) or organic-inorganic (distribution of Fe₃O₄ particles in organic film).

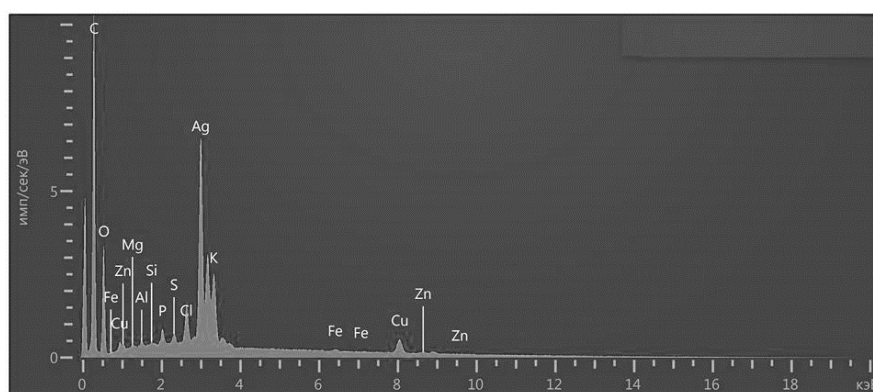
The helical fiber bundles of TL sample look like blossoming flower buds, the thickness of “petals” is several microns (Fig. 2 *c*). After modifying, the bundles are covered with a films, extraneous inclusions are visible (Fig. 2 *d*).

Tapering-expanding bundles with branches are seen in the SEM image for the PW sample, their thickness is 10–50 μm (Fig. 2 e). The cracked film with holes is seen on the surface of PW-Fe

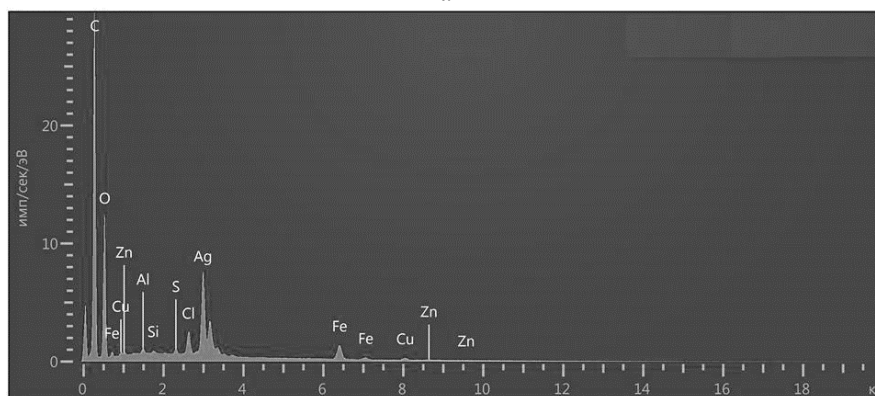
(Fig. 2 e). At last, keratin matrix consists of flakes (up to 15 μm, Fig. 2 g). The structure of flakes becomes denser after modifying, the film is also visible (Fig. 2 h).

Table 1. Chemical composition of initial biopolymers

Element	Element content, mass %			
	CC-0	TL-0	PW-0	DW-0
C, line of K-series	45.23	61.92	57.51	44.55
O, line of K-series	22.02	20.64	28.34	14.15
Ag, line of L-series	23.25	13.53	12.48	14.66
Cl, line of K-series	1.11	-	0.09	-
Cu, line of K-series	4.04	0.94	0.87	0.92
K, line of K-series	2.49	-	0.19	-
P, line of K-series	0.51	0.13	0.06	-
S, line of K-series	0.32	0.14	-	5.37
Al, line of K-series	0.17	0.18	0.18	0.14
Zn, line of K-series	0.44	0.31	-	0.16
Mg, line of K-series	0.12	0.19	-	-
Fe, line of K-series	0.24	-	-	-
Si, line of K-series	0.06	0.07	-	-
Ca, line of K-series	-	1.84	0.27	0.61
W, line of L-series	-	0.12	0.01	-
Na, line of K-series				0.35
N, line of K-series				19.08
Total	100.00	100.00	100.00	100.00



a



b

Fig. 1. Electronic spectra of CC (a) and CC-Fe (b) samples

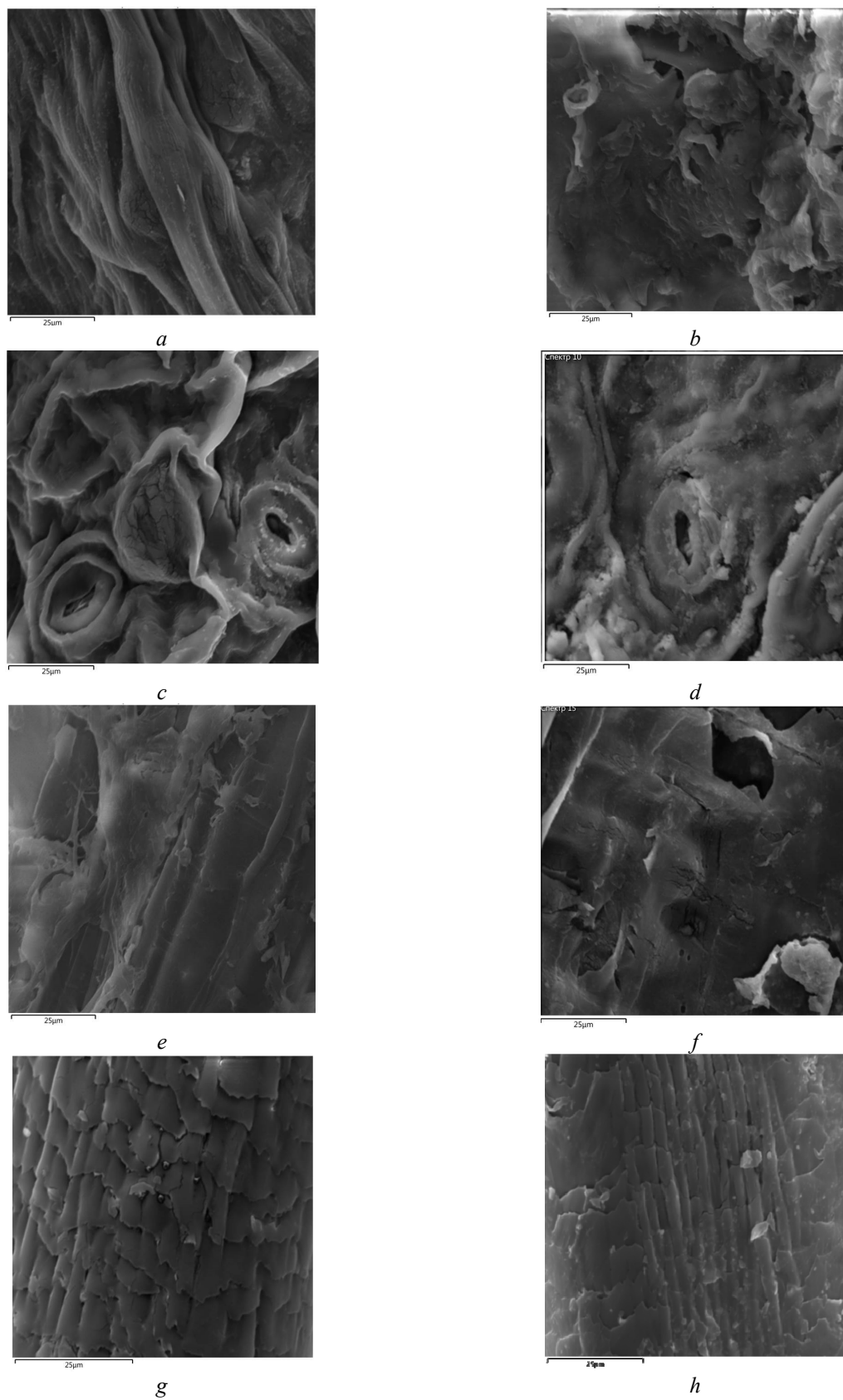


Fig. 2. SEM images of CC (a), CC-Fe (b), TL (c), TL-Fe (d), PW (e), PW-Fe (f), DW (g), DW-Fe (h) samples

The most heterogeneous distribution of the modifier particles is achieved in the case of CC-Fe sample (Fig. 3 *a*). The particle size is mainly less than 1 μm . Regarding other samples, significant concentrations of particles is observed (Figs. 2 *b-d*), the regions of Fe distribution looks even continuous (TL-Fe). These “islands” are irregular with “swirls” (TL-Fe, PW-Fe) or as a narrow straight tracks (DW-Fe). It means, the

film, which is observed in Fig. 2 *b*, is organic-inorganic, where magnetite particles are homogeneously distributed. At the same time, magnetite fills the space between spiral wall of the TL-Fe samples, it is also distributed in a film. The PW-Fe and DW-Fe samples occupy intermediate positions. Indeed, the Fe content decreases in the order: TL-Fe > DW-Fe > PW-Fe > CC-Fe.

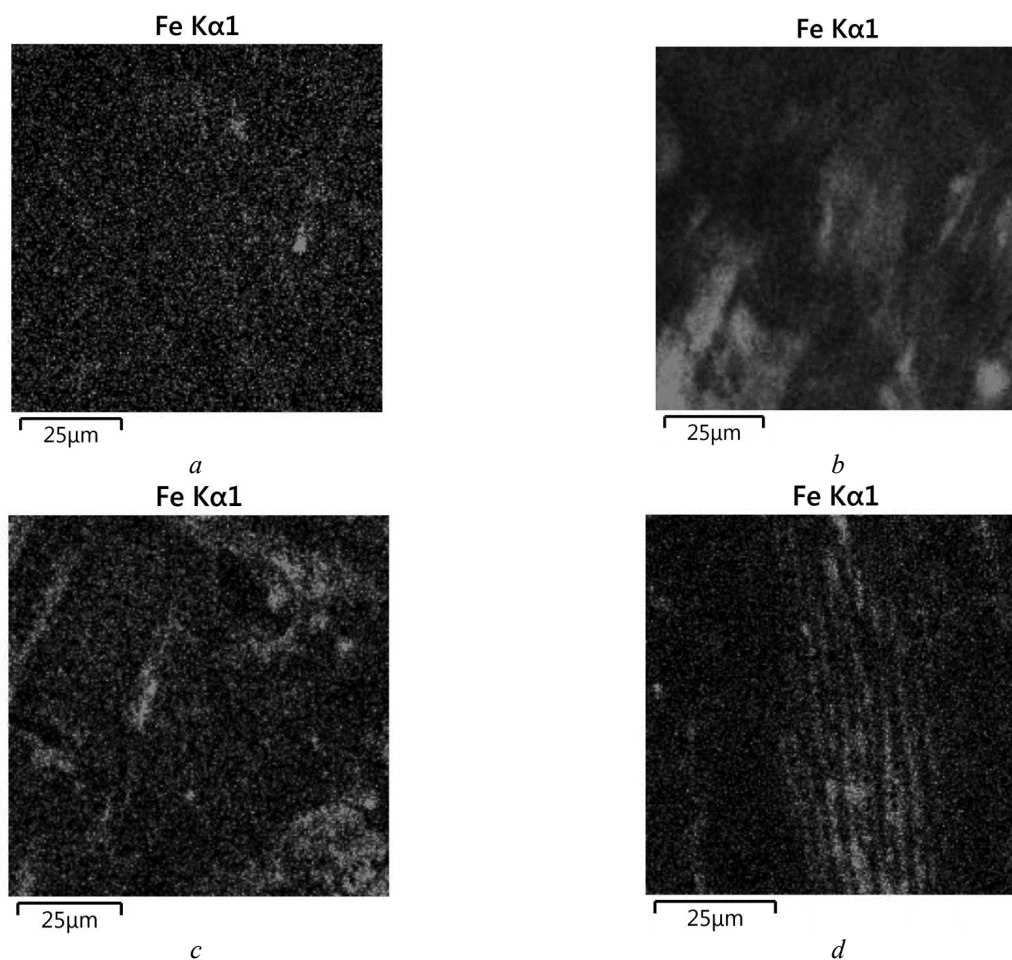


Fig. 3. Maps of Fe distributions through the CC-Fe (*a*), TL-Fe (*b*), PW-Fe (*c*), DW-Fe (*d*)

Table 2. Fe content in the composite samples and their sorption characteristics

Parameter	CC-Fe	TL-Fe	PW-Fe	DW-Fe	
Fe content, mass %	0.24	71.02	4.36	5.73	
Flotation, %	95	3	88	85	
Capacity towards non-polar liquids, $\text{g}\cdot\text{g}^{-1}$	vegetable oil	6.90	1.64	7.17	8.58
	crude oil	10.56	14.58	15.10	16.37
	kerosene	9.82	12.96	12.30	14.52
COD for water after the removal of crude oil, $\text{mgO}_2 \text{ dm}^{-3}$	0.25	–	0.2	0.2	

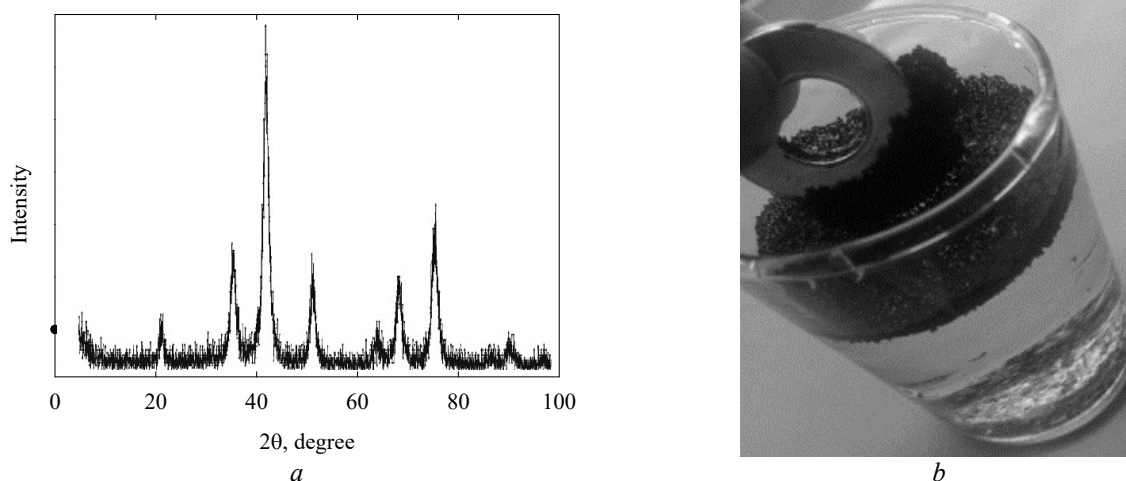
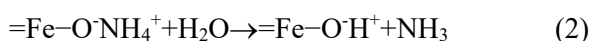


Fig. 4. XRD pattern for the magnetite sample (a), removal of DW-Fe particles from water surface (b)

Fig. 4 a illustrates typical XRD pattern for the synthetic magnetite sample (JCPDS Card No. 79–0417). The structure is related to spinel. The diffraction peaks are located at $2\theta = 21^\circ$ (indexed to (111)), 35° ((220)), 41° (311), 50° (400), 63° (422), 67° (511) and 75° (440). The samples modified with magnetite show magnetic properties: their particles are removed with magnet from the water surface (Fig. 4 b). Even the samples containing a small amount of the modifier, for instance Cer-Fe, are capable to be attracted to magnet. However, some sorbent particles sink to the vessel bottom evidently under the influence of heavy modifier, which performs a function of load. Air pores are filled with water and the sorbent particles sink. Indeed, the order of flotation (i.e. the ratio of mass of floating and all sorbent particles) coincides with the order of Fe content (see Table 2). However, hard particles can be considered as sorbents for removal of inorganic ions.

According to the Fe_3O_4 composition, the mass ratio of Fe and O is 2.94. However, lower iron content has been found. According to chemical analysis, this ratio is 2.62. This difference is due to water content in magnetite. Indeed, FTIR spectrum shows characteristic stripe in the region of $4000\text{--}3000\text{ cm}^{-1}$ (Fig. 5 d). The peak at 1620 cm^{-1} is also caused by O–H vibration, the stripe at 1519 cm^{-1} is due to vibration of Fe–O–H groups, which are formed during rinsing magnetite after precipitation using ammonia solution:



The bands at $< 1000\text{ cm}^{-1}$ are attributed to vibrations that are characteristic namely to Fe_3O_4 [43]. The peak at 553 cm^{-1} is due to Fe–O vibration, when Fe atoms in tetrahedral position. At the same time, Fe in octahedral positions gives the band at 443 cm^{-1} .

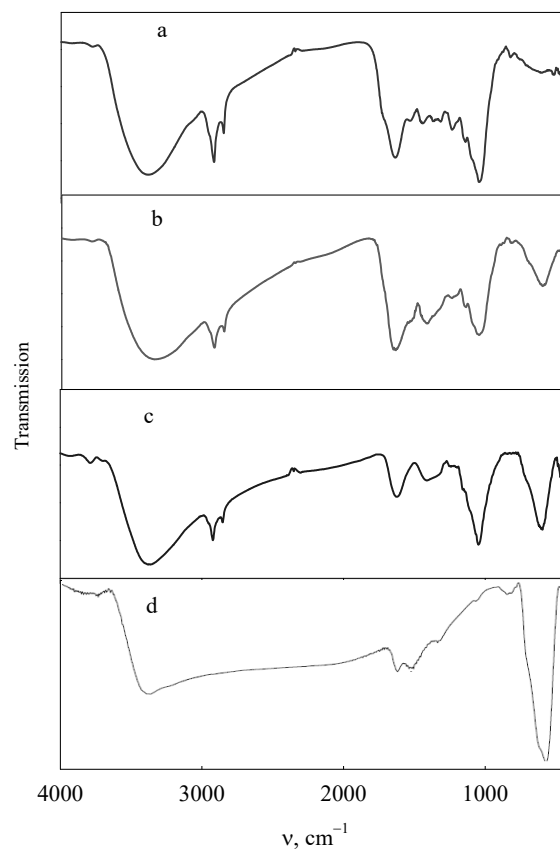


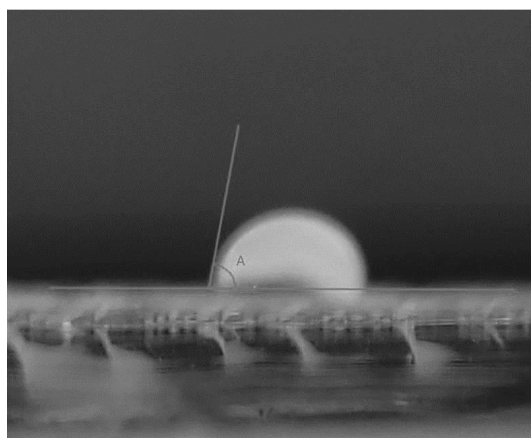
Fig. 5. FTIR spectra for the samples CC-0 (a), CC-Fe (b), TL-Fe (c), magnetite (d)

FTIR spectra allows us to identify also functional groups of the non-modified samples. As an example, Fig. 5a illustrates the spectra for the CC-0 sample. The region of 4000 to 1900 cm^{-1} gives no useful information, since valence vibrations of O-H and C-H groups are realized in this frequency interval [44]. Maximum at 1638 cm^{-1} is related to C=O fragments of carboxyl groups, the shoulder at 1735 cm^{-1} and the peak at 1568 cm^{-1} are due to the vibrations of carbonyl fragments of these groups. Carboxyl groups are slowly formed during the decomposition of cellulose under aerobic conditions. The degradation is carried out by a number of bacteria, actinomycetes and fungi [45]. The low intensive peaks at 1334 and 1158 cm^{-1} are related to the δ vibrations of

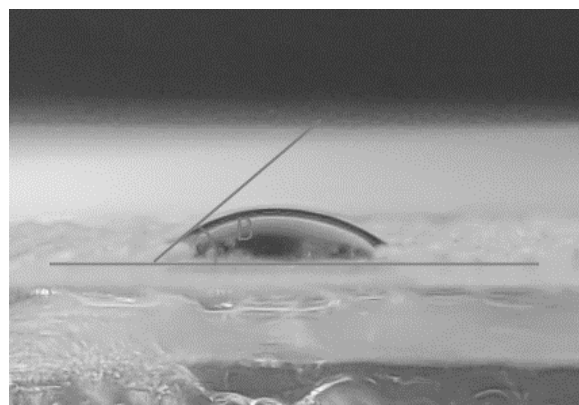
C-O-H groups, the band at 1460 cm^{-1} is attributed to the δ vibrations of O-H groups [42]. The intensive band at 1048 cm^{-1} is caused by valence C-O-C vibrations.

As opposed to non-modified samples, the composites demonstrates peaks, which are characteristic for the inorganic constituent, especially in the region of 1000–400 cm^{-1} (Figs. 5 b, c). The data are additional confirmation of Fe_3O_4 location in biopolymer matrices.

The water contact angle for the corn sample is approximately 100 degrees, while the oil contact angle is approximately 30 degrees, which is evidence of hydrophobicity and oleophilicity of the corn sample (Figs. 6 a, b).



a



b

Fig. 6. Wetting angle for water (a) and oil (b) of the corn sample

Sorption capacity of the samples towards non-polar liquids is given in Table 2. The samples show the lowest capacity towards vegetable oil, the highest values were found for crude oil. The order of capacity is $10 \text{ g} \cdot \text{g}^{-1}$. As mentioned above, higher capacity values can be achieved, however, the synthesis process is complicated by additional hydrophobization of biopolymer matrices. Moreover, magnetite particles containing surface –OH groups provide hydrophylyzation of matrices, which are free from hydrophilic non-cellulose and non-keratin inclusions.

When crude oil was removed from water surface, the CC-Fe sorbent, which is originally light yellow, was painted black, i.e. color of this liquid (Fig. 7). After the removal of oil from water surface (Fig. 7), no film of non-polar liquid was

visually observed in aqueous media. However, the COD value was higher comparing with that for deionized water ($\ll 0.2 \text{ mg} \cdot \text{O}_2 \text{ dm}^{-3}$). This is due to formation of oil emulsion in water during stirring. Nevertheless, the COD parameter is suitable even for drinking water ($< 0.3 \text{ mg} \cdot \text{O}_2 \text{ dm}^{-3}$).

The part of the sorbent that sinks in water, was applied to the removal of toxic inorganic ions from water. Fig. 8 illustrates typical sorption isotherms for Pb^{2+} and Cd^{2+} ions for the samples based on cellulose obtained from corn cobs. As seen, the modifier increases sorption capacity towards Pb^{2+} ions and decreases it towards Cd^{2+} ions. In general, the capacity value was within the interval of 0.06–0.11 (Cd^{2+}) and 0.13–0.25 (Pb^{2+}) $\text{mmol} \cdot \text{g}^{-1}$, when the concentration of initial solutions was $0.01 \text{ mmol} \cdot \text{dm}^{-3}$. Similar results were obtained

for other sorbents (Table 3) and also for natural zeolite modified with Fe-containing constituent

[46]. The reason of this phenomenon requires further investigations.



Fig. 7. Removal of crude oil from water surface with CC-Fe sample

Table 3. Sorption capacity (mmol g^{-1}) of non-modified and modified biopolymers towards inorganic ions (sorption from 0.0001 M solutions)

Ions	CC-0	CC-Fe	TL-0	TL-Fe	PW-0	PW-Fe	DW-0	DW-Fe
Pb^{2+}	0.017	0.020	0.011	0.015	0.012	0.017	0.010	0.014
Cd^{2+}	0.008	0.005	0.005	0.002	0.007	0.005	0.006	0.004

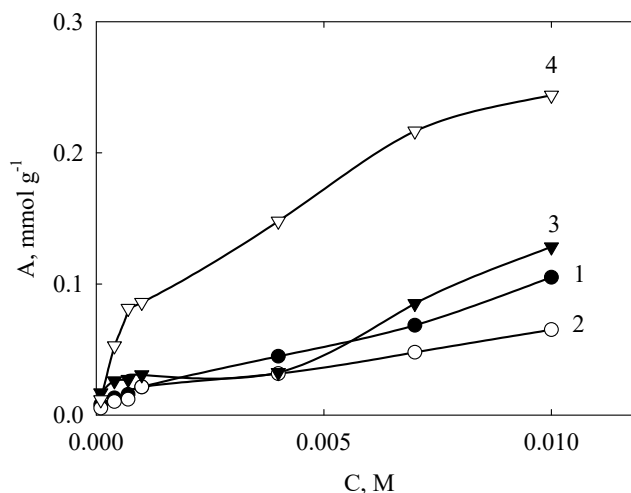


Fig. 8. Isotherms of Cd^{2+} (1, 2) and Pb^{2+} (3, 4) adsorption for the CC-0 (1, 3) and CC-Fe (2, 4) samples

CONCLUSIONS

Magnetic sorbents, which were obtained from biopolymers of plant and animal origin, can be recommended for the removal of oil and oil products from water surface. The sorbents synthesized using cellulose of corn cobs and wood, as well as the material based on wool

keratin are most suitable for this purpose, since they demonstrate the best flotation. The CC-Fe sorbent, which shows no flotation, can be applied for the removal of Pb^{2+} ions from water. Despite lower capacity towards non-polar liquids in comparison with the materials, which contain specially inserted hydrophobic component [47],

biopolymer-based sorbents are characterized by a number of advantages. First of all, it is a simple preparation procedure that involves cheap and available feedstock, namely wastes of agriculture industry and salts of Fe(II) and Fe(III).

Moreover, the sorbents can be easily separated from aqueous phase with magnet. Sorbents partially sink in water, this fraction can be preliminarily separated from the floated particles and used for the removal of toxic inorganic ions.

Сорбенти на основі біополімерів різної природи, що містять магнетит, для видалення нафтопродуктів та токсичних іонів з води

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Нафта і нафтопродукти потрапляють до поверхневих вод внаслідок техногенних катастроф, спричинених, зокрема, військовими діями. Для запобігання негативних екологічних наслідків вуглеводні мають бути видалені з водних поверхонь. У статті представлено результати розробки матеріалів для вилучення неполярних рідин із водних середовищ. Запропоновано магнітні сорбенти на основі некарбонізованих біополімерів (рослинної целюлози і кератину). Для виготовлення композитів використовували біополімерні матриці різної морфології на рівні пучків волокон. Залежно від походження матриці, пучки волокон є прямими (целюлоза, отримана з деревини та кукурудзяних качанів), спіралеподібними (целюлоза чайного листя) або лускатими (кератин вовни тварин). Частинки магнетиту вводили до біополімерних матриць після видалення з них нецелюлозних і некератинових включень. Зразки досліджували методами СЕМ та Фур'є ІЧ спектроскопії, магнетит ідентифікували за допомогою рентгенофазового аналізу. Найбільш однорідний розподіл магнітних частинок, розмір яких менший за 1 мкм, виявлено для матриці, отриманої з качанів кукурудзи. Цей композит містив найменшу кількість заліза (0.24 мас. %): саме цей зразок демонструє найкращу плавучість. Сорбент на основі целюлози з листя чаю містив 71% заліза: частинки тонули у воді майже повністю. Його ємність за неполярними рідинами становила ($g\ z^{-1}$): 1.6–8.6 (рослинна олія), 10.5–16.4 (нафта), 9.8–14.5 (гас). Після видалення з поверхні води сирої нафти, плівка цієї рідини візуально не спостерігалася. Для очищеної води хімічне споживання кисню становило $\approx 0.2\ mgO_2\text{-}dm^{-3}$, це менше норми для питної води. Крім того, сорбент можна легко видалити з водної поверхні за допомогою магніту. Встановлено, що сорбенти також можна використовувати для видалення з води іонів токсичних металів. Як виявлено, магнітні частинки покращують сорбцію іонів Pb^{2+} , але зменшують сорбцію Cd^{2+} . Таким чином, сорбенти з невеликим вмістом неорганічного модифікатора можуть бути використані для видалення нафти і нафтопродуктів з водних поверхонь. Для вилучення неорганічних іонів можна використовувати сорбенти, які тонуть у воді. Перевага сорбентів на основі біополімерів перед відомими матеріалами полягає у нескладному способі синтезу, який передбачає використання дешевої та доступної сировини. Крім того, сорбенти можна легко відокремити від води за допомогою магнітного поля.

Ключові слова: біополімери, магнетит, магнітний композит, нафта, нафтопродукти, очищення води

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