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REMOVAL IONS OF FERRUM(III) AND ZINC FROM AQUEOUS ENVIRONMENTS BY CHEMICALLY ACTIVATED SORBENTS FROM NATURAL RAW MATERIALS

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Abstract

The process of purifying model solutions from heavy metal iron(III) and zinc ions with sorbents of natural origin from secondary raw materials was studied. In the work, a number of experiments on the activation of natural sorbents were carried out. To activate zeolite, mineral acids HNO_3, HCl, and H_3PO_4 were used, and lignocellulosic sorbent from walnut shells was activated with HNO_3 and treated with an acid-salt solution containing 20 % H_3PO_4, 40 % $CO(NH_2)_2$, and 40 % H_2O. The activation of the sorbents was carried out by technological operations of impregnation, washing with distilled water to pH = 7–8, and drying at a temperature of 130 °C. The finished sorbents were tested for effectiveness by extracting heavy metal Fe(III) and Zn from water systems. Comparative characteristics of cellulose-containing sorbent with mineral zeolite are given. It was established that the use of chemically activated lignocellulosic sorbent is more effective for the extraction of heavy metals in comparison with acid-activated zeolite. The optimal duration of of the lignocellulosic sorbent with the adsorb ate is 3 hours, while the cleaning efficiency for Fe(III) is 82.5 %, and Zn is 84.65 %. The optimal dose of lignocellulosic sorbent was established, which was 1 g/dm^3. A mathematical description of the kinetics of the iron (III) sorption process on a lignocellulosic sorbent in the 283 – 293 K temperature range was performed. It was established that the process of extracting heavy metals takes place in the diffusion region, the activation energy for Fe(III) is 41.22 kJ/mol, Zn – 34.36 kJ/mol. The advantages of the lignocellulosic sorbent are characterized by its cheapness, selectivity, cation exchange properties for removing heavy metals, and its use in the sorption purification of water systems at industrial enterprises given.

Keywords: zeolite; walnut shell; lignocellulosic sorbent; chemical activation; mineral acids; heavy metals; ferrum (III); zinc.

ВИЛУЧЕННЯ ІОНІВ ФЕРУМУ(ІІІ) ТА ЦИНКУ ІЗ ВОДНИХ СЕРЕДОВИЩ ХІМІЧНО АКТИВОВАНИМИ СОРБЕНТАМИ ІЗ ПРИРОДНОЇ СИРОВИНИ

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Анотація

Досліджено процес очищення модельних розчинів від іонів важких металів феруму(ІІІ) та цинку сорбентами природного походження із вторинної сировини. У роботі проведено ряд експериментів з активації природних сорбентів. Для активації цеоліту використано мінеральні кислоти HNO_3, HCl, H_3PO_4, лігноцелюлозний сорбент із шкарлупи волоського горіху активовано HNO_3 та оброблено кислотно-сольовим розчином, який містив 20 % H_3PO_4, 40 % $CO(NH_2)_2$, і 40 % H_2O. Активацію сорбентів здійснено шляхом технологічних операцій просочування, промивання дистильованою водою до pH = 7–8, та сушки при температурі 130 °С. Готові сорбенти перевірено на ефективність вилучення іонів важких металів Fe(III) та Zn із водних систем. Наведено порівняльну характеристику целюлозовмісного сорбенту з мінеральним цеолітом. Встановлено, що використання хімічно активованого лігноцелюлозного сорбенту є ефективнішим для вилучення важких металів у порівнянні із кислотно активованим цеолітом. Оптимальною тривалістю контактування лігноцелюлозного сорбенту з адсорбатом є 3 год, за якої досягається ефективність очищення для Fe(III) – 82.5 %, Zn – 84.65 %. Встановлено оптимальну дозу лігноцелюлозного сорбенту, що складає 1 г/дм^3. Виконано математичне описання кінетики процесу сорбції феруму(ІІІ) та цинку на лігноцелюлозному сорбенті в інтервалі температур 283–293 К. Встановлено, що процес вилучення важких металів протікає у дифузійній області, енергія активації становить для Fe(III) – 41.22 кДж/моль, Zn – 34.36 кДж/моль. Наведено переваги сорбенту із лігноцелюлози, що характеризуються його дешевизною, селективністю, катіонообмінними властивостями для видалення важких металів та дозволяє застосовувати в технології сорбційного очищення водних систем на промислових підприємствах.

Ключові слова: цеоліт; шкарлупа волоського горіха; сорбент лігноцелюлозний; хімічна активація; мінеральні кислоти; важкі метали; ферум(ІІІ); цинк

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Introduction

Formulation of the problem. In connection with the intensive growth and development of industry, the influx of heavy metals of man-made origin into the environment has increased significantly in recent years, including Fe(III) and Zn [1].

Harmful pollutants enter water bodies together with sewage, worsening their sanitary condition and causing the need for special deep water purification before using it for household needs.

Wastewater, entering reservoirs, changes the composition of natural water and negatively affects the ecological system. In order for the composition of wastewater not to destroy the ecosystem, it is necessary to carry out effective cleaning [2].

Anthropogenic pollution of the environment with heavy metals poses a great danger to the biosphere. In addition to the direct toxic effect on living and plant organisms, heavy metals accumulate in food chains, increasing their danger to humans. When they get into water bodies, they are in the most dangerous form for a long time, and even when they change to a bound state (colloidal form) or other poorly soluble compounds, they continue to represent a potential threat [3].

Industrial liquid waste from chemical in dustries, contaminated with heavy metal ions, can cause great, irreparable damage to the environment even at small concentrations. The discharge of wastewater into reservoirs sharply worsens their overall sanitary condition, having a negative impact on living organisms not only with its high toxicity but also with a significant change in the mode of consumption of biogenic elements and dissolved gases. Removing heavy metals is a difficult task because they often have a low concentration. Heavy metals have the ability to have various chemical, physical and chemical reactions, move, redistribute, and migrate.

Minimizing the negative anthropogenic impact on water bodies is possible by improving existing and developing new methods and technologies for extracting pollutants from liquid waste, including heavy metals.

To clean sewage from heavy metals, adsorption methods are used, which are based on the sorption of pollution molecules under the influence of a force field in the pores of the adsorbent. Non-carbon sorbents of natural origin are increasingly used.

The use of these sorbents is due to their sufficiently high adsorption capacity, selectivity, cation exchange properties, relatively low cost, and availability. The most important representatives of natural mineral sorbents are clay materials [4; 5].

They are quite common and differ in a variety of properties and areas of application. Natural sorbents are extracted directly near the place of use, which constantly expands the limits of their application for wastewater treatment [6–8].

Clay aluminosilicate minerals are promising sorbents for wastewater treatment from heavy metal ions. Natural clay minerals are inferior in adsorption characteristics to zeolite. The disadvantage of natural clay minerals is their small capacity, which is for metal cations within the following limits, MML/l: 0.163 (Fe^{3+}); 0.11–0.16 (Zn^{2+}). Sorption methods are widely used for cleaning industrial wastewater, but there are several problems in this field, the most significant of which include: insufficient sorption capacity of materials, low selectivity of sorbents, and utilization of heavy metals from waste. One of the approaches is the synthesis and use of composite sorbents based on natural minerals and polymers, as well as synthetic polymer materials, selective for heavy metal ions and insensitive to other ions, such as hardness salts. Extraction of residual amounts of organic pollutants can be intensified by combining oxidation with the water sorption method [9; 10].

Montmorillonite and aqueous calcium and sodium aluminosilicates arepromising sorbents for water purification. They have a porous three-dimensional structure of tetrahedral. Zeolites are crystalline, porous aluminosilicates with a framework. The three-dimensional classical frame of zeolite is built from the main building blocks – tetrahedral [SiO_4] and [AlO_4], the vertices of which relate to the help of oxygen elements. The negative charge of the tetrahedral compensates for the cations of alkaline and alkaline earth cations located in the zeolite. The composition of zeolite can be described by the formula:

$$Me_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O,$$

where n is the valence of the alkali metal cation, x is the SiO_2/Al_2O_3 molar ratio, and y is the number of moles of water.

The growing interest in sorbents from natural raw materials is also due to the need to replace traditional methods of cleaning water environments with ecologically harmless ones. The peculiarity of the purification of the water environment is the introduction of the stage of sorption purification into the complex technological scheme of water treatment. As a rule, this stage is the final stage in the technological process of cleaning water systems. Carbon and mineral sorbents of natural origin are increasingly used for water purification by adsorption. One type of biomass is a walnut shell [12].

In recent years, numerous publications have appeared focusing on the evaluation of walnut shells. A significant part of them focuses on their use for obtaining sorbents in water purification technology. The use of shell-based sorbents is due to their sufficiently high adsorption capacity, selectivity, cation exchange properties, and low cost and availability.

Analysis of recent research and publications. The latest technologies are intensively developing, and the secondary processing of industrial waste is more often used all over the world. Ukraine is one of the top 5 walnut producers in the world. The production volume of which in 2022 was at the level of 133 thousand tons. Therefore, there is a problem with the storage and disposal of the shell formed after processing this nut [13].

The shell is difficult to decompose and pollutes the environment. Therefore, a promising direction is the use of this biomaterial as a carbon sorbent. The chemical composition of walnut shells consists of lignin (35.0 %), cellulose (30.4 %), polysaccharides (12 %), and hemicellulose (12.6 %). The most characteristic functional groups of lignocellulosic materials - OCH_3 (up to 22 %), carboxyl -COOH (up to 16 %), carbonyl =CO (up to 7 %), hydroxyl (alcohol and phenolic) -OH (up to 11 %). Lignin is a ball-shaped, thermoplastic polymer with a mesh structure [14].

Low molecular weight lignin is insoluble, and it is extremely difficult to isolate it from the polymeric structures of plants in its pure form without low molecular weight and polymeric impurities. The organic component is 78–97 % of dry matter. The average molecular weight of lignin depends on the type of raw material and the method of its extraction, and is in the range of 800–11,000 a.o.m. The sorption activity of lignin and cellulose can be increased by appropriate chemical modification with acids, alkalis, oxides, etc. As a result of such processing, materials acquire high reactivity, easily enter into addition and substitution reactions, and can perform the functions of selective sorbents or ion exchangers [15]. When carbon sorbents are obtained from walnut shells, their carbonization or pyrolysis is carried out. Carbonization is the thermal destruction of the source material without access to oxygen in the temperature range of 500 and 1000 °C. During carbonization, the carbon content increases to 95 % by weight. The purpose of carbonization is to create primary porous structures that will further develop during the activation process. After the carbonization stage, the material becomes porous. In order to expand its porous structure and make its surface more reactive, it must undergo a second stage of heat treatment, called activation. Activation allows the creation of porous microstructures and increases the accessibility of the internal structure, as well as creating new pores and expanding the diameter of those already created in the carbonization process [16; 17].

There are three types of activation. Steam-gas (physical) activation consists of the oxidation of coal at high temperatures with the help of an oxidizer for 24 to 72 hours. For this, gaseous reagents are used: water vapor (H_2O), carbon dioxide (CO_2), or oxygen (O_2). All these gases can be used separately or in a mixture. When using water vapor, the activation process proceeds with a reaction rate at a temperature of about 800 °C, and when using carbon dioxide, the temperature is raised to 900 °C. With the mixed method of coal activation, after chemical activation, it is additionally subjected to physical activation (at a high temperature). Chemical activation is carried out in the presence of hydrochloric, phosphoric, sulfuric, nitric acids, sodium, and potassium hydroxides, while the raw materials are impregnated with these chemical agents [18].

In previous studies [19], we carried out acid activation of zeolite HNO_3, HCl, H_3PO_4 and checked its effectiveness in extracting methyl blue dye. The efficiency of using an acid-activated sorbent for the extraction of dyes from wastewater was verified. The kinetic regularities of the process of adsorption of dyes in the contact with natural and activated zeolite were established, in the time interval every 6 hours for 24 hours. It is recommended to use natural adsorbent zeolite - activated by hydrochloric acid with a concentration of 4 g/dm^3 with a contact time of 24 hours, under these technological parameters, the dye content decreases from 117 mg/dm^3 to 41 mg/dm^3. Based on the high sorption indicators of activated zeolite, it is advisable to check its efficiency in relation to the extraction of metals [20]. Researches of experimental comparison of chemically activated zeolite and lignocellulosic sorbent from a walnut shell on its effectiveness in purifying model solutions from heavy metal ions (Fe(III) and Zn) are interesting.

Formulation of the purpose of the research. The purpose of this work is to study the process of adsorption extraction of Fe(III) and Zn metals from model solutions by lignocellulosic sorbent from walnut shell and acid-activated zeolite.

It is recommended to use natural adsorbent zeolite – activated by hydrochloric acid with a concentration of 4 g/dm^3 with a contact time of 24 hours, under these technological parameters, the dye content decreases from 117 mg/dm^3 to 41 mg/dm^3. Based on the high sorption indicators of activated zeolite, it is advisable to check its efficiency in relation to the extraction of metals.

Materials and methods of the research

Lignocellulosic sorbent (LCS) from natural raw materials (walnut shells) was prepared as follows: the material was first crushed, classified and fractions of 0.6–1.6 mm size were selected. Then the sorbent was treated with a 57 % HNO_3 solution for 4 hours with constant stirring. Next, the solid phase was washed with distilled tap water to pH = 7–8 and dried at a temperature of 130 °C for 3 hours. Further, the mixture was treated with an acid-salt solution containing 20 % H_3PO_4, 40% $CO(NH_2)_2$, and 40 % H_2O, with constant stirring for 4 hours (this ratio of the components of the working solution is the most effective and enables the activation of raw materials at room temperature temperature – 15–25 °C).

After activation, the mixture was filtered again, separating the filtrate into a separate container, and the sorbent was conditioned by soaking in water for 6 days. Then the water was returned to wash the sorbent. After activation, cellulose and lignin cease to be bound into biopolymer complexes characterized by high sorption and ion exchange properties. Since cellulose contains hydroxyl groups in each elementary chain, they can react with heavy metals.

To compare the sorption properties of lignocellulosic sorbent, previously activated mineral sorbent – zeolite was used. As an activator, 7 % solutions of mineral acids HNO_3, HCl, H3PO4 were used. Acid activation was carried out according to the following method. Three heat-resistant flasks were loaded with zeolite, which was treated with a 7 % solution of HNO_3, HCl, H_3PO_4 acids in a ratio of 1 : 2. The activation time lasted 4 days with periodic stirring. Immediately after activation with an acid solution, three samples of the activated sorbent were washed with distilled water until the pH was neutral. Next, the sorbent was dried first in a water bath until air-dry, and then in a drying cabinet at a temperature of 130 °C for 3 hours.

Activation by acids allows you to release and clean the micro- and mesopores of the main zeolite matrix. Cleaning the pores leads to an increase in the porosity of the zeolite and improves its sorption properties. Acid activation is the most beneficial procedure, which removes accompanying elements (Al, K, Na, Ca, Mg) and cleans micropores and does not lead to destruction of the zeolite structure.

In order to identify the most effective sorbent and optimal technological parameters for its industrial implementation, the obtained chemically activated sorbents were used for the purification of liquid media from heavy metals, namely Fe(III) and Zn.

Experimental part

For the extraction of heavy metals (Fe(III) and Zn) from model solutions, lignocellulosic sorbent and three samples of zeolite activated with 7% nitric, chloride, and orthophosphoric acids were tested. Table 1 presents the chemical composition of the lignocellulosic sorbent.

Table 1

Chemical composition of lignocellulosic sorbent

№	Component	Formula	Concentration, % wt.
1	Cellulose	$(C_6H_{10}O_5)_n$	42.8
2	Lignin	$(C_{10}H_{12}O_3)_n$	29.5
3	Hemicellulose (pentosans and hexosans)	$(C_5H_8O_4)_n$	18.7
4	Silicon oxide	SiO_2	9.0

Table 2 shows the chemical composition of a sample of zeolite that was activated by acids. The chemical composition of the zeolite sample activated by acids is shown in Table 2.

The porosity of the zeolite is 45 %, the pore diameter is 1 nm, and the cation exchange capacity is 1.18 mg·eq/g.

Table 2

Chemical composition of zeolite

Oxide	Content, wt.%	Oxide	Content, wt.%
Al_2O_3	13.1	CaO	2.1
SiO_2	69.7	Fe_2O_3	0.9
Na_2O	4.38	MnO_2	1.07
K_2O	1.37	TiO_2	0.2

For experimental studies, 8 heat-resistant flasks, 8 magnetic stirrers, 4 types of sorbents (lignocellulosic, zeolite activated by chloride, orthophosphate, and nitric acids) were used. The initial concentration of Fe(III) and Zn in the model solutions was 200 mg/dm^3.

The concentration of the heavy metal working solution of 200 mg/dm^3 was chosen for the following reasons. The average indicator of heavy metals in wastewater is for cyanide wastewater: 5–80 mg/dm^3; chromic – 50–100 mg/dm^3; acidic and basic – 100–200 mg/dm^3 [21]. The goal of the work is to achieve the extraction rate of Fe(III) and Zn ions of ≈ 80 % at a high concentration (200 mg/dm^3).

Working solution was taken in 1–4 heat-resistant flasks, and 200 ml of Zn working solution was taken in 5–8 flasks, and activated sorbents were added at the rate of 1 g/dm^3 (0.2 g per 200 ml of aqueous solution). Water purification from heavy metal ions lasted 4 hours with constant stirring on magnetic stirrers. Samples were taken every hour to analyze the residual concentration of metals in the water. To determine heavy metals, 50 ml of the tested water was taken from a flask with a capacity of 200 ml with a measuring cylinder and an indicator was added, sulfalicylic acid was used for Fe^{3+} ions and 2 dm^3 of ammonium acetate was added. It was also titrated with a standard solution of EDTA (ethylenediaminetetraacetic acid ($(HOOCCH_2)_2N(CH_2)_2N(CH_2COOH)_2$) until the color changes from red to transparent at pH 5–6.

In the presence of an indicator for Zn^{2+} ions, 1 g of xylene orange was used, which was triturated with 99 g of KNO_3 and 2 dm^3 of ammonium acetate was added. It was then titrated with a standard EDTA solution (ethylenediaminetetraacetic acid ($(HOOCCH_2)_2N(CH_2)_2N(CH_2COOH)_2$) until the color changes from purple to yellow at pH 2.5. Based on the obtained data, graphs of the dependence of the residual concentration of Fe(III) and Zn on the adsorption time were constructed (Figs. 1, 2).

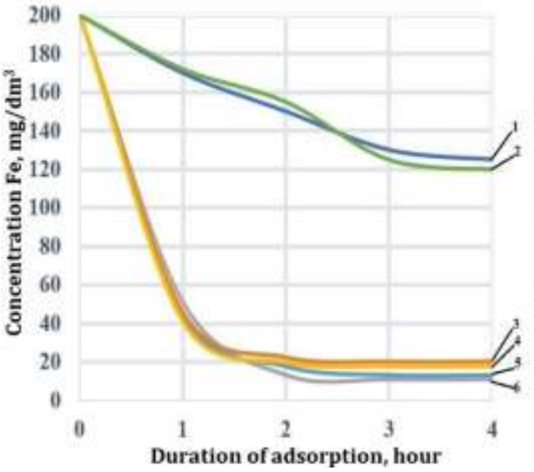

Fig. 1. Dependence of the residual Fe(III) concentration on the adsorption time at a sorbent consumption of 1 g/dm^3: 1 – zeolite is not activated; 2 – lignocellulosic sorbent is not activated; 3 – zeolite activated by H_3PO_4; 4 – zeolite activated by HNO_3; 5 – zeolite activated by HCl; 6 – lignocellulosic sorbent

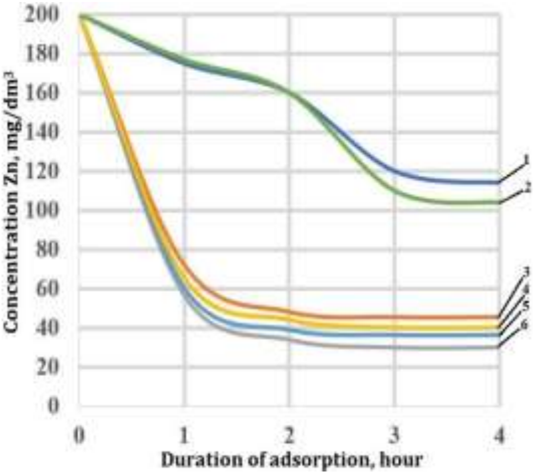

Fig. 2. Dependence of the residual concentration of Zn ions on the adsorption time at a sorbent consumption of 1 g/dm^3: 1 – zeolite is not activated; 2 – lignocellulosic sorbent is not activated; 3 – zeolite activated by H_3PO_4; 4 – zeolite activated by HNO_3; 5 – zeolite activated by HCl; 6 – lignocellulosic sorbent

It was established that with a sorbent consumption of 1 g/dm^3, after 1 hour of contact when using a lignocellulosic sorbent, the content of Fe(III) decreases from 200 to 31.27 mg/dm^3, Zn – from 200 to 36.6 mg/dm^3; the content of Fe(III) in zeolite activated by hydrochloric acid decreases to 24.56 and Zn to 40.52 mg/dm^3; activated by nitric acid – Fe(III) up to 21.21 and Zn up to 45.75 mg/dm^3; activated by orthophosphate acid - Fe(III) up to 25.68 mg/dm^3 and Zn up to 52.29 mg/dm^3.

With an increase in the contact time to 3 hours, the residual concentration of Fe(III) and Zn is as follows: when using a lignocellulosic sorbent for Fe(III) – 11.16 mg/dm^3; Zn – 30.7 mg/dm^3; zeolite activated by hydrochloric acid – Fe(III) – 13.4 mg/dm^3; Zn – 36.6 mg/dm^3; zeolite activated by nitric acid – Fe(III) – 17.86 mg/dm^3; Zn – 40.52 mg/dm^3; zeolite Fe(III) activated by phosphoric acid – 20.1 mg/dm^3; Zn – 45.75 mg/dm^3. On the basis of the conducted experimental research, it was established that the chemically activated lignocellulosic sorbent turned out to be the most effective in relation to the extraction of Fe(III) and Zn ions. The optimal contact time of sorbents with aqueous solutions of heavy metal salts is 3 hours, after 4 hours of the experiment the residual concentration of Fe(III) and Zn ions did not change. Therefore, there is no technological need to keep the solution for more than 3 hours.

Cellulose is considered a weakly acidic ignite (pKa(RCOOH) ≈ 4.0 and pKa(ROH) ≈ 9.2, but there is no consensus on the mechanism of metal sorption by it. The swelling and sorption activity of cellulose samples depends on the ratio of the regions of the amorphous and crystalline structure in them, which, in turn, it is determined by the raw materials that went into their production. We assume that the sorption of heavy metals by modified lignocellulosic sorbents is determined by the nature of the sorption centers of hydroxyl and carboxyl groups of the lignocellulosic material and electron-donating N-, S-, and P-containing groups grafted as a result of chemical modification

Activation by acids allows removing elements from the zeolite structure, freeing and cleaning the micro- and mesomorphs of the main zeolite matrix. Cleaning the pores leads to an increase in the porosity of the zeolite and improves its sorption properties. Acid activation does not destroy the zeolite structure.

At the next stage, the influence of LCS consumption on the residual concentration of metals was investigated and graphs of the dependence of the concentration of Fe(III) and Zn on the influence of LCS in the range of 0.5–1.5 g/dm^3 were drawn (Figs. 3, 4).

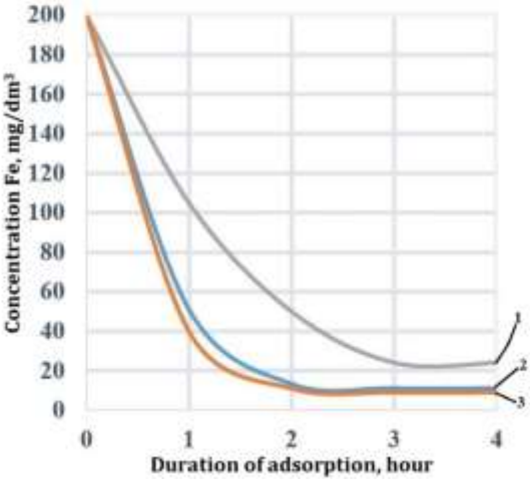

Fig. 3. Graph of dependence of Fe(III) concentration on LCS dose: 1 – 0.5 g/dm^3; 2 – 1 g/dm^3; 3 – 1.5 g/dm^3

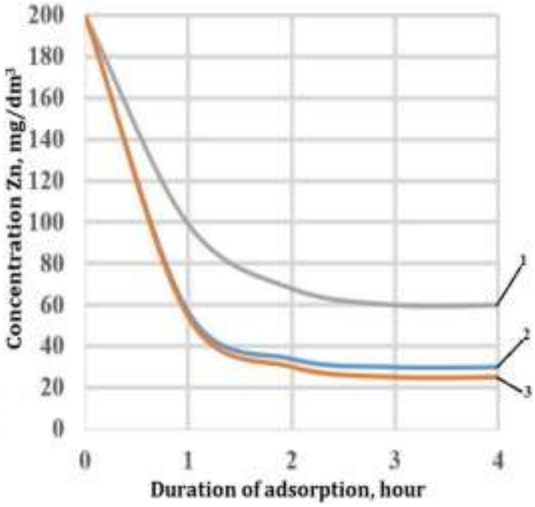

Fig. 4. Graph of the dependence of the concentration of Zn ions on the dose of LCS: 1 – 0.5 g/dm^3; 2 – 1 g/dm^3; 3 – 1.5 g/dm^3

It was established that with a sorbent consumption of 0.5 g/dm^3 after 4 hours of contact when using LCS the content of Fe(III) decreases from 200 to 24 mg/dm^3; Zn – from 200 to 60 mg/dm^3. When the sorbent consumption is increased by 2 times (1 g/dm^3), the content of Fe(III) decreases from 200 to 11.6 mg/dm^3, Zn – from 200 to 30.7 mg/dm^3. Much better results were obtained when using a sorbent with a dose of 1.5 g/dm^3, the content of Fe(III) decreased from 200 to 9 mg/dm^3, Zn from 200 to 25 mg/dm^3.

From Fig. 3, it can be observed that after the first hour, the efficiency of cleaning liquid media from Fe(III) ions at a sorbent consumption of 0.5 g/dm^3 is 50.5 %; 1 g/dm^3 –71.7 %; 1.5 g/dm^3 – 87.5 %. The extraction rate of Zn ions (Fig. 4) at a sorbent consumption of 0.5 g/dm^3 is 47.5%; 1 g/dm^3 – 74.36 %; 1.5 g/dm^3 – 80 %.

Therefore, increasing the concentration of the sorbent affects the efficiency of metal extraction. The sorbent consumption of 0.5 g/dm^3 is more economically beneficial, but the cleaning performance is insufficient. It was established that the degree of removal of heavy metals at the consumption of SLC of 1 g/dm³ and 1.5 g/dm³ is close in terms of indicators, therefore, from an economic point of view, it is recommended to use LCS with a concentration of 1 g/dm³.

In order to identify the kinetic parameters of adsorption, namely the rate constants and activation energy, the effect of temperature on the efficiency of Fe(III) and Zn extraction from SCL was investigated in the range 283–293 K at a sorbent consumption of 1 g/dm³ (Figs. 5, 6). The adsorption activation energy depends on the interatomic distances in the adsorbed molecules and on the surface; according to their favorable ratio, Ea can be minimal.

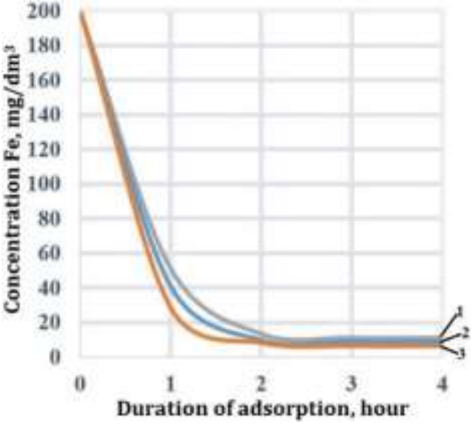

Fig. 5. Effect of temperature on the efficiency of Fe(III) extraction at a sorbent consumption of 1 g/dm³: 1 – 291 K; 2 – 297 K; 3 – 303 K

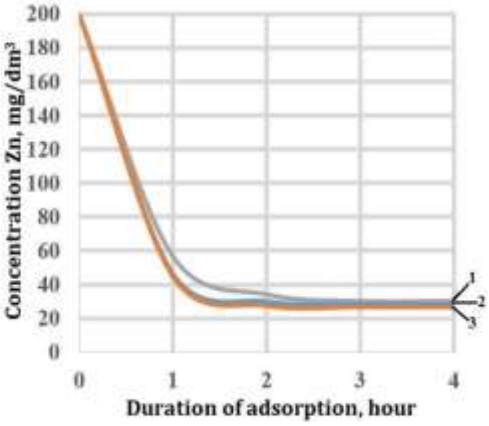

Fig. 6. Effect of temperature on the extraction efficiency of Zn ions at a sorbent consumption of 1 g/dm³: 1 – 291 K; 2 – 297 K; 3 – 303 K

From fig. 5, 6 it can be seen that when the temperature increases from 283–293 K, the sorption rate increases already after the 1st hour of contact. The concentration of Fe(III) decreased from 51.27–28.52 mg/dm³, which is 22.75 mg/dm³ lower, and Zn from 56.6–44.8 mg/dm³ – by 11.8 mg/dm³, respectively.

As the temperature rises, the rate of sorption increases, because the share of active collisions increases.

The values of the kinetic parameters of the Fe(III) and Zn sorption process on LCS with a flow rate of 1 g/dm³ are shown in Table 3.

Table 3

The value of the kinetic parameters of the Fe(III) and Zn sorption process on LCS with a flow rate of 1 g/dm³

Temperature of the aqueous solution , K	Sorption rate constant k		Process order n L		Sorption constants ln k	
	Zn	Fe(III)	Zn	Fe(III)	Zn	Fe(III)
283	$1.98 \cdot 10^{-3}$	$3.59 \cdot 10^{-3}$	1.4	1.4	–8.5	–7.9
288	$1.37 \cdot 10^{-3}$	$2.88 \cdot 10^{-3}$	1.5	1.4	–8.9	–8.1
293	$1.23 \cdot 10^{-3}$	$1.99 \cdot 10^{-3}$	1.5	1.5	–9.0	–8.5

In fig. 7, 8 shows the dependence of the logarithm of the rate constant of the Fe(III) and Zn sorption process (k) on 1/T in the temperature range of 283–298 K. The activation energy was found analytically and graphically using the Arrhenius equation in a linear form.

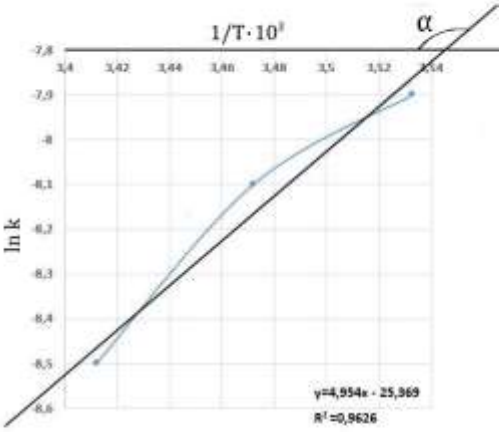

Fig. 7. Dependence of the logarithm of the rate constant of the Fe(III) sorption process (k) on LCS on 1/T in the temperature range 283–298 K

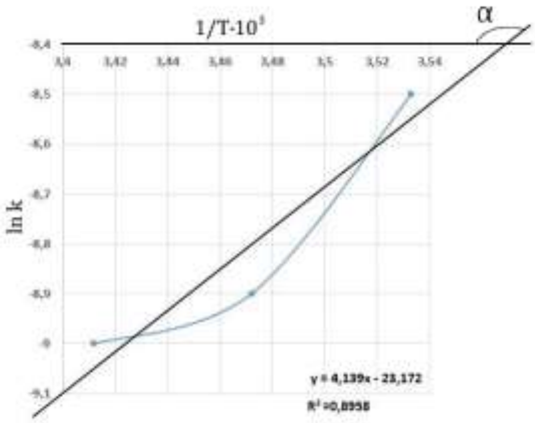

Fig. 8. Dependence of the logarithm of the rate constant of the Zn(k) ion sorption process on LCS on 1/T in the temperature range 283–298 K

The dependence of the rate constant of the Fe(III) sorption process on LCS (Fig. 7) on the temperature in the range of 283–298 K is described by the equation of a straight line: ln k = 4.954·1/T – 25.369.

The activation energy is determined using the formula:

$$E_a = -\frac{ln_{k2} - ln_{k1}}{\frac{1}{T_2} - \frac{1}{T_1}} * R$$

From fig. 7 the activation energy is 41/22 kJ/mol.

The dependence of the rate constant of the process of removal of Zn ions on LCS (Fig. 8) on the temperature in the range of 283–298 K is described by the equation of a straight line:
ln k = 4.139·1/T – 23.172.

From fig. 8 the activation energy is 34.36 kJ/mol.

The experimental value of the activation energy of Zn and Fe(III) sorption on LCS was 34.36–41.22 kJ/mol, which indicates a diffusion-limited process. Thus, the absorption of pollutants by the surface of a solid adsorbent is carried out due to the interaction of pollutant molecules with the surface of the adsorbent and subsequent diffusion of molecules of substances through the film surrounding the particles of the adsorbent to its surface, the speed of which is determined by the structure of the adsorbent, the presence of pores and the size of the molecules of the adsorbed substance.

Conclusions

Chemically activated sorbents based on zeolite and walnut shell were obtained. Walnut activation was carried out with the participation of chemical agents (57 % HNO_3 solution, acid-salt solution containing 20 % H_3PO_4, 40 % $CO(NH_2)_2$, and 40 % H_2O) and drying at a temperature of 130 °C. As a zeolite activator, 7 % solutions of mineral acids HNO_3, HCl, H_3PO_4 were used. Acid activation of sorbents was carried out by the infiltration method. The concentration of heavy metals in model solutions was determined by the titrimetric method.

Samples of chemically activated zeolite and lignocellulosic sorbent were compared for their effectiveness in cleaning model solutions from heavy metals (Fe(III) and Zn). It was established that the use of chemically activated lignocellulosic sorbent is more effective for the extraction of heavy metals than acid-activated zeolite.

The optimal technological parameters for the sorption of Fe(III) and Zn metals on a lignocellulosic sorbent were found, namely, a contact time of 3 hours. The residual concentration of Fe(III) from 200 mg/dm^3 to 11.16 mg/dm^3 (cleaning efficiency was 82.5 %) and Zn from 200 mg/dm^3 to 30.7 mg/dm^3 (cleaning efficiency was 84.65 %) was achieved), with a sorbent consumption of 1 g/dm^3.

A mathematical description of the kinetics of the sorption process of Fe(III) and Zn ions by a lignocellulosic sorbent with a flow rate of 1 g/dm^3 in the temperature range of 283–293 K was performed, and it was established that the process of extraction of heavy metals takes place in the diffusion region, the activation energy for Fe(III) is 41.22 kJ/mol, Zn – 34.36 kJ/mol, which indicates the absorption of iron(III) and zinc by the modified sorbent due to the interaction of pollutant molecules with its surface and subsequent diffusion of substance molecules through the film surrounding the adsorbent particles to its surface, the speed of which is determined by the structure of the adsorbent, the presence of pores and the size of the molecules of the sobbed substance. Based on the values of the activation energy for this natural sorbent, it can be assumed that the limiting stage of the adsorption process of heavy metal ions is chemical interaction.

Thus, for the removal of Fe(III) and Zn metals from aqueous solutions, lignocellulosic sorbent showed greater efficiency compared to acid-activated zeolite. The advantage of the lignocellulosic sorbent is also due to its cheapness, because biomass, including walnut shells, is a production waste. The activated sorbent is characterized by selectivity, and cation exchange properties for the removal of heavy metals, which allows it to be used in the technology of sorption purification of water systems at enterprises. The perspective of further research is the experimental determination of optimal conditions for the sorption of other heavy metals by lignocellulosic sorbent and production tests.

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