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FEATURES OF ADSORPTION PROCESSES FOR WASTEWATER TREATMENT FROM ZINC IONS

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Abstract. The results of adsorption properties of complex natural sorbents in relation to the neutralization of zinc ions from wastewater are presented. The adsorption isotherm of Zn^{2+} ions on complex sorbents (clinoptilolite-shungite) (1:1) according to Langmuir and Freundlich models is constructed, the type of adsorption isotherms according to S. Brunauer classification is established. The value of the maximum sorption capacity of Gmax complex sorbents for Zn^{2+} ions is calculated. The peculiarities of the sorption process of zinc ions with the formation of a monomolecular layer based on the calculated coefficients of the Langmuir and Freundlich were found. The optimal conditions for the dependence of the degree of absorption of Zn^{2+} ions by complex sorbents on the duration of the sorption process are determined. The ratio "solid (complex sorbent) – liquid" was determined experimentally.

Key words: ecological safety, natural sorbents, sorption isoterma, wastewater adsorption.

1. Introduction

One of the main tasks of environmental protection is to prevent the ingress into wastewater the soil cover components that contain heavy metal ions in concentrations higher than the maximum allowable. Heavy metal ions have an extremely negative effect on living organisms since they have cumulative and toxic properties, complicate the operation of natural and wastewater treatment stations in populated areas.

Today, according to experts, with insufficiently purified industrial wastewater, thousands of tons of highly toxic heavy metals, such as zinc – 3.3 thousand tons, nickel – 2.4 thousand tons, chromium – 0.5 thousand tons and others annually fall into natural water facilities, greatly complicating the environmental situation in the country. The main sources of receipt of these components, as a rule, are industrial facilities with a developed industrial base and a wide range of technological processes and operations, in particular, the aviation industry, which uses the latest methods of material processing, introduces promising technologies, etc. However, we should not forget the scale of environmental pollution with heavy metal ions thrown into the trash of spent batteries.

The most famous and common "finger" batteries contain a lot of manganese and zinc (23–28 % is contained in salt lead batteries), a little less – some other heavy metals and chemical elements.

Approximately 2.500 tons of batteries are imported to Ukraine annually, but only 1 % of them are recycled. The batteries thrown by us on garbage get to a landfill of household waste. There, as a result of various organic reactions and corrosion, harmful chemical compounds from batteries get directly into the environment. They pollute water bodies, soil, and due to plants get into food chains.

Numerous scientific publications of domestic and foreign scientists are devoted to the extraction of zinc ions from liquid solutions and the study of the sorption mechanism (Bolshanina et al., 2013; Yang et al., 2014; Zhang et al., 2009; Pshinko et al., 2015; Zhang et al., 2014; Repo et al., 2011).

It is known that the most promising method of wastewater treatment is sorption technology, which is widely used in various industries. Currently, considerable experience has been gained in the use of natural clay minerals and their modified forms for wastewater treatment from heavy metal ions.

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The prospect of using natural minerals in the process of effluent purification is confirmed not only by their high adsorption capacity, but also by the existence of effective methods for improving the adsorption properties of minerals and the nature of their surface by modification (Malovanyy et al., 2013; Sydorchuk, Humnytskyi, 2013; Petrushka et al., 2013; Petrushka et al., 2019).

However, considering the selectivity of natural minerals, a significant number of scientists are working to improve the sorption properties of sorbents by modifying them or using complex mineral sorbents.

In addition to traditional natural sorbents (clinoptilolite, paligorskite, glauconite), which are used to treat wastewater from heavy metal ions, shungite rocks are no less interesting in terms of sorption capacity.

Shungite is a rock that includes silicon dioxide. The mineral has become widespread in various areas of human activity, in construction and metallurgy. But the physicochemical properties of shungite are so unique that the rock began to be used in unconventional medicine and for water purification. In nature, the mineral is formed as a bottom deposit of organic origin. Shungite is a transition stage of graphite, which determines the dark color of the rock. Minerals of gray and brown shades are less common (Shpylevsky et al., 2001; Berezkin, 2013).

Shungite rocks are unique in composition, structure and properties. They are an unusual structure natural composite – a uniform distribution of finely dispersed crystalline silicate particles in an amorphous carbon matrix. Rocks are characterized by high strength, density, chemical stability and electrical conductivity. They have a number of unusual physical, chemical, physicochemical and technological properties [8, 9].

The bulk (up to 99 %) of the shungite is represented by non-crystalline carbon, the defining feature of which is the globular structure. It is based on a ball – a hollow multilayer formation with dimensions up to 10 nm. The noticeable curvature of the graphite layers allowed the authors to conclude about the fullerene-like structure of shungite carbon (Shpylevsky et al., 2001).. Mineral components are represented by fine crystals (from 1 to 10 microns) of mica, quartz, albite, etc. Such a structure makes it possible to consider shungite as a natural composite material and provides for the possibility of its developing unique sorption properties (Berezkin, 2013).

An important task in studying the sorption properties of sorbents is the process of modeling and predicting the mechanism of absorption of pollutants from liquid media (Sydorchuk, Humnytskyi, 2013; Petrushka et al., 2013; Petrushka et al., 2019).

Therefore, studies aimed at reducing the anthropogenic load on the environment by improving the adsorption properties of sorbents in wastewater treatment from used batteries containing mercury, cadmium, lead, tin, nickel, zinc, magnesium and others are relevant and important for improving the environmental safety of water environment.

The purpose of the work is to increase the level of environmental safety of the hydrosphere by increasing the sorption ability of complex natural sorbents when cleaning the liquid medium from Zn^{2+} ions.

2. Experimental part and Results

Analysis of adsorption isotherms indicates that the adsorption process in many cases is not limited to the formation of a monolayer of deposition and even at relatively low values of the relative pressure P/Ps≈0.1, as a rule, polymolecular layers are formed. Brunauer, Demming, Demming, and Teller (BDDT) identified five main types of gas adsorption isotherms on solid adsorbents.

The founder of the monomolecular model of physical adsorption was Langmuir. According to the concept developed by him, the adsorption layer consists of molecules localized on the exponential surface that do not interact with each other. Lateral interactions in Langmuir's theory are not taken into account.

Most adsorption systems are characterized by the form of the Langmuir and Freundlich isotherm. A characteristic feature of this type of isotherm is that at a certain value of the concentration of the component in the liquid medium, the equilibrium concentration in the solid phase reaches a value that can be considered almost constant.

In order to obtain an optimal ratio between sorbents (clinoptilolite – schungite), experimental studies of their sorption ability relative to (Zn^{2+}) were carried out.

To obtain a uniform granulometric composition of complex sorbents, they were first ground in a laboratory bullet mill with steel layers, then by the method of hearth analysis, they were adjusted to a uniform granulometric composition with a grain size of 0.3 mm.

The experimental determination of the adsorption value and the degrees of extraction of components from the solution was determined by the dependencies (1,2):

$$G = \frac{(C_{initial} - C_{equilibrium})}{m_{sorb}} \cdot W \; ; \qquad (1)$$

$$\alpha = \frac{(C_{initial} - C_{equilibrium})}{C_{initial}} \cdot 100 \ \% \qquad (2),$$

where $C_{initial}$ and $C_{equilibrium}$ is the initial and equilibrium concentration of the component in solution (mg/dm^3); m_{sorb} is the mass of sorbent (g); W is the volume of solution (l).

In practice, the empirical Freundlich equation is used for analysis and calculations:

$$G = \beta \cdot C^{1/n} \tag{3},$$

where β and $1/n$ are the constants; $C_{equilibrium}$ is the equilibrium concentration (mg/dm^3).

The constants of the Freudlich equation are found when logarithmizing equation (3) and constructing a graphical dependence:

$$gG = lg\beta + \frac{1}{n} lgC \tag{4}$$

To determine the maximum adsorption (G_{max}), the dependence 1/G = f (1/C) is built, which allows to determine G_{max}, which corresponds to the complete saturation of the surface layer of the adsorbent.

Based on the prepared model solutions, isotherms of adsorption of Zn^{2+} on natural and complex sorbents were obtained (Fig. 1)

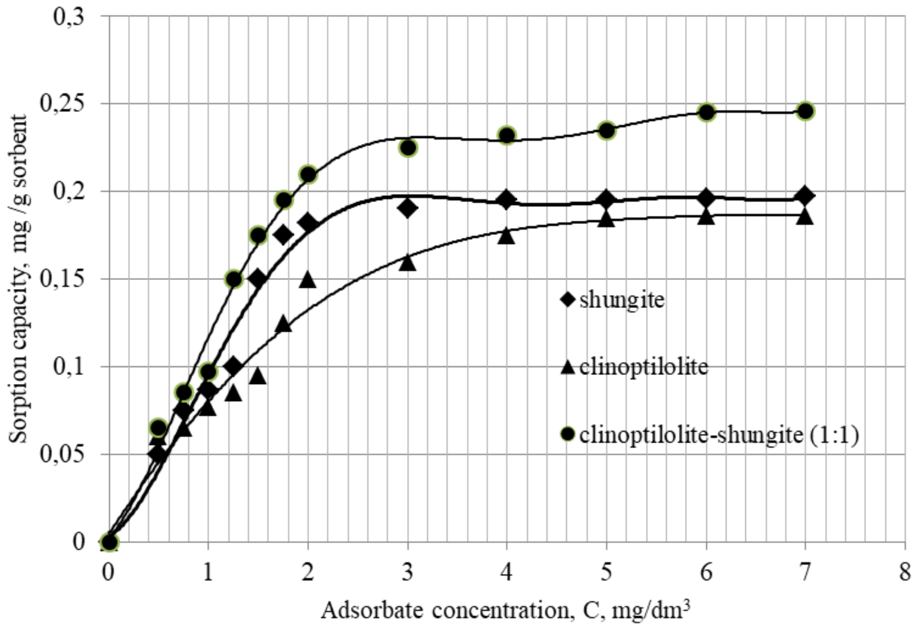

Fig. 1. Adsorption isotherms of Zn^{2+} by natural complex sorbents

From the above graphic data, it can be seen that the complex sorbent – "clinoptilolite-shungite" has the greatest sorption ability in relation to Zn^{2+} in static conditions at a ratio of 1:1, respectively.

In order to establish the main parameters of the intensity of adsorption processes and determine the type of adsorption isotherm, we interpreted the experimental data within the theoretical models of Langmuir and Freundlich.

The obtained adsorption isotherms of Zn^{2+} on complex sorbents (Fig. 2) belong to type 1 according to the classification of S. Brunauer, with a characteristic bend relative to the concentration axis at the initial stage of sorption followed by plateau formation, which characterizes the end of the sorbent surface saturation period.

Comparing the values of the approximation (R2) (Table 1), it was found that the obtained experimental data are described with sufficient accuracy by the Freundlich equation and with less accuracy by the Langmuir equation, which in both cases indicates that sorption occurs with the formation of a monomolecular layer. High values of the coefficient of determination indicate a significant chemical inhomogeneity of the surface of complex sorbents, which causes uneven distribution of active centers on the surface of materials and affects the degree of the adsorption layer filling (Table 1).

The calculated coefficients of the Langmuir and Freundlich equations indicate the nature of the process of Zn^{2+} ions sorption by the value of the maximum sorption capacity and selectivity of sorbents.

Within the study of the adsorption properties of complex sorbents based on clinoptilolite and shungite on zinc ions, it was found that to achieve the maximum purification at the minimum cost of sorption material, the required ratio "solid – liquid" is 1:25. The mass of the sorbent was 10, 20, 25 and 30 g /dm^3. The dynamics of changes in the concentration of Zn^{2+} ions (Cinitial = 2.0 mg/dm^3) from the time of interaction of the model solution with the natural sorbent is shown in Fig. 3.

The obtained results indicate that the optimal sorption conditions are observed at a solid-liquid ratio of 1:30. It was found that when the concentration of the sorbent increases several times, the degree of extraction increases only by 2–9 % and does not exceed 90.5 % of the initial concentration.

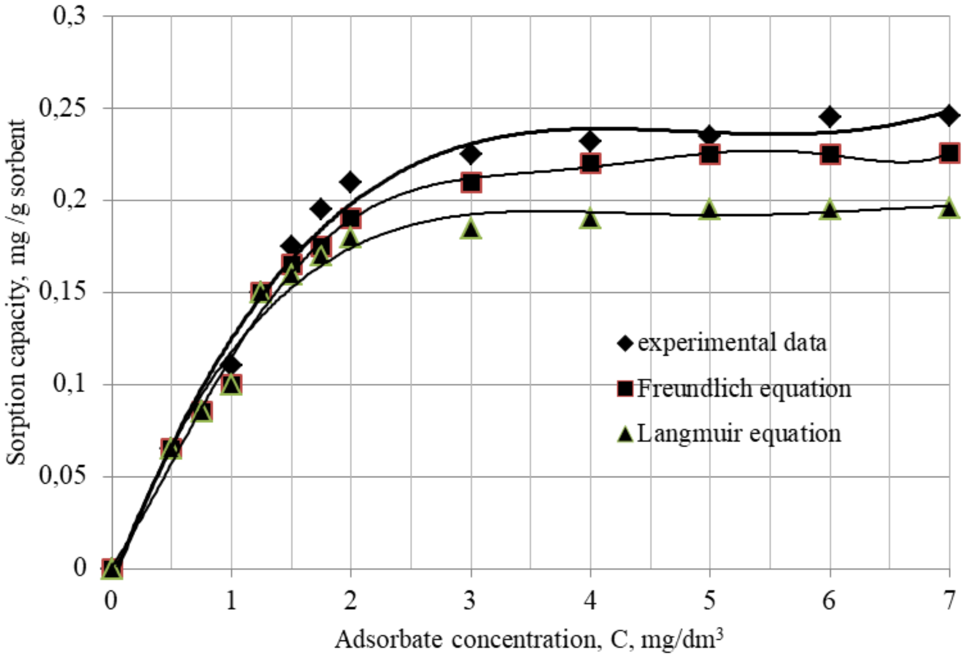

Fig. 2. Sorption isotherm of zinc by a complex sorbent (clinoptilolite-shungite -1: 1) according to the results of the experiment, according to the equations of Freudlich and Langmuir

Table 1

Parameters of Zn^{2+} adsorption isotherms with complex sorbent

Adsorbate	Langmuir equation			Freundlich equation		
	Amax, mg/g	*K_L*	R^2	*в*, mg/g	*1/n*	R^2
Activated bentonite-shungite (1: 1)						
Zn^{2+}	0.2473	1.4765	0.9144	0.11689	0.285	0.9728

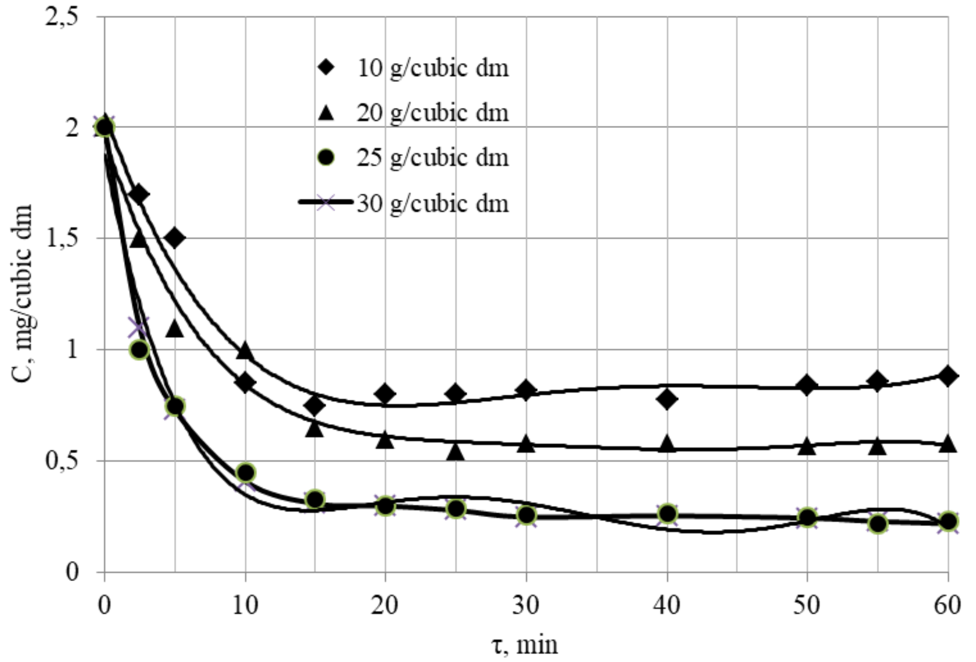

Fig. 3. Change in the concentration of Zn^{2+} ions in solution at different concentrations of complex sorbent: 10 g/dm^3; 20 g/dm^3; 25 g/dm^3; 30 g/dm^3

As the experiments showed, the sorbent concentration of over 30 g/dm^3 does not lead to a significant decrease in the concentration of Zn^{2+} ions. It was found that the optimal amount of clay material of 25 g/dm^3 for 5 minutes reduces the zinc concentration from 2 mg/dm^3 to 0.23 to 0.06 mg/dm^3. As a rule, the sorption process stabilizes for 45 minutes, after which there is no significant decrease in the concentration of Zn^{2+} ions.

3. Conclusions

Comparative characterization of adsorption isotherms of Zn^{2+} ions on complex sorbents (clinoptilolite-schungite (1:1) according to the models of Langmuir and Freundlich was carried out, their type was determined according to the classification of S. Brunauer. The value of the maximum sorption capacity of Gmax sorbents relative to Zn^{2+} ions was set, which is 0.23 mg/g. The calculated coefficients of the Langmuir and Freundlich equations made it possible to establish the nature of the sorption process of Zn^{2+} ions in the monomolecular layer of the complex sorbent.

It was established that in the sorption of ions and Zn^{2+} on a complex sorbent, the ratio "solid substance – liquid" is 1:25, while the maximum concentration decrease is observed already for 5–10 minutes of the purification process and is almost 84 %, and after 30 minutes the sorption process stabilizes, after which a significant decrease in the concentration of Zn^{2+} ions does not occur.

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