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Sorption Extraction of Heavy Metal Ions from Wastewater by Natural and Synthetic Sorbents

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East Kazakhstan region is the center of non-ferrous metallurgy of the Republic of Kazakhstan. There are large metallurgical enterprises in the region that pollute ground and surface waters with heavy metals. Wastewater treatment of large enterprises, which include Ust-Kamenogorsk metallurgical complex "Kazzinc", is an urgent problem. Among the chemical and physical-chemical methods of purification, sorption is very advantageous due to the opportunity to seal and neutralize the waste. Sorbent of different nature for purification of the given metallurgical complex wastewater is used in the work: natural material – shungite, activated by chlorhydric acid and water; polymer-protected hydrogel with embedded particles of activated shungite. Polymer-protected hydrogel is a cross-linked polymer based on acrylamide and N,N'- methylene- polyacrylamide, bis-acrylamide. Preliminary tests were carried out on model solutions in order to determine the optimal contact time of the sorbent with the solution. Static conditions were chosen to obtain higher values of extraction coefficients. Studies conducted on real wastewater have shown that the most effective sorbent is a polymer-protected hydrogel with activated shungite particles. Shungite is easily introduced into the polymer in the mixing process and requires less energy consumption for distributing in the polymer. Mineral and carbon parts of shungite can be introduced nearly into all polar and nonpolar polymers that is due to the components contained in shungite (noncrystalline carbon and silicon dioxide with hydrophilous and hydrophobic properties), due to metastability of shungite carbon structure, as well as possibility to change surface characteristics during chemical modification.

1. Introduction

Large metallurgical enterprises are concentrated in the East Kazakhstan region. The main polluter is Ust-Kamenogorsk metallurgical complex "Kazzinc". The level of contamination of underground and surface waters within the boundaries of the pollution area exceeds that of zinc and copper. The increasing scale of production and requirements for water quality dictate the search for more effective ways to purify natural and wastewater, and to recycle treated wastewater for reuse. Traditional methods of wastewater treatment, for example, as a reagent method, do not provide deep purification of wastewater from metal ions (Menshova et al., 2016). Among the methods used for deep treatment of non-ferrous metallurgy wastewater from heavy metal ions, the sorption method is the most effective one. The advantages of sorption method are the following: high sorption capacity; selectivity factor; comparatively low cost, availability, as it is local material; process control and possibility to remove contaminants of different nature up to any residual concentration independent of their chemical resistance (Corda et al., 2019). Purification of wastewater from non-ferrous metallurgical enterprises by using new sorbent materials is a relevant problem nowadays.

For wastewater treatment, various artificial materials (Srisuwan et al., 2018) such as activated carbon (Cali et al., 2019), polymeric membranes (Gnanaselvan et al., 2019) and natural materials are used as sorbents (Guixia et al., 2014): zeolites (Aubakirova et al., 2018), shungites (Fischer et al., 2018), bentonite clays (Daumova et al., 2018) and others. Synthesis of sorbents with a high sorption capacity that can effectively absorb various metal ions from wastewater is of interest (Mamyachenkov et al., 2017).

Comparison of physical and chemical characteristics (porosity, chemical and thermal stability, sorption capacity) of shungites with other natural sorbents (bentonite clay, zeolite) enables to forecast their effective

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use in the processes of sorption extraction of metals from process solutions (Yergozhin *and* Akimbaeva, 2007). Despite of considerable number of papers devoted to zeolites, and bentonite clays, they are not commonly used as catalysts for polymers, due to complex and multistage technology of their synthesis (Romanenko *and* Yeliseyeva, 2018). Fullerenes (shungites) are used as catalysts and initiators of polymerization reaction, as fullerite crystal is a molecular crystal, transition form between organic and non-organic substance (*Ignatov,* 2018). Shungite is easily introduced in the mixing process, requires less energy consumption for distribution in the polymer. Shungite is activated by acids solutions, often by chlorhydric acid solution for providing higher sorption characteristics (Akimbaeva et al., 2010).
In this work the possibility of using natural and synthetic sorbents is considered for the treatment of heavy metals from wastewater of metallurgical enterprises on the example of the Ust-Kamenogorsk metallurgical complex "Kazzinc".

2. Materials and methods

2.1 Materials and their preparation for the experiment

Experimental research on wastewater purification from heavy metals ions was carried out by using a natural sorbent - shungite of Bakyrchik deposit of East Kazakhstan and polymer-protected hydrogel obtained by polymerization reaction from Acrylamide and other monomers and introduction of activated shungite particles into hydrogel for synthesis of polymer-shungite complex.

2.1.1 Shungite, composition and properties

Shungite carbon is a fossilized ancient oil, or amorphous, non-crystallizing, fullerene-like carbon that contains certain regular structures. Its content in the rock is about 30 %, and there is 70 % of silicate minerals-quartz, mica. In addition to carbon, shungite also includes SiO_2 (57.0 %), TiO_2 (0.2 %), Al_2O_3 (4.0 %), FeO (2.5 %), MgO (1.2 %), K_2O (1.5 %), S (1.2 %). Shungite carbon forms a matrix in the rock where dispersed silicates with an average size of about 1 μm are evenly distributed. The properties of shungite rock are determined by two factors: first, the properties of shungite carbon, and second, the structure of the rock, the relationship of carbon and silicates (Efremov et al., 2013). Shungite has a high activity in redox processes, sorption and catalytic properties and it is in close contact with the silicates contained in it. The particles of shungite, regardless of their size, possess bipolar properties. This results in high adhesion and shungite ability to mix with all substances without exception (*Ignatov and Mosin*., 2014). Physical properties of shungite: density - 2.25-2.40 g/cm^3; porosity - 0.5-5 %.

2.1.2 Preparation of activated shungite

The essence of the method is based on rubbing shungite stone and sifting through sieves, followed by processing in two ways: hydrochloric acid or water. Shungite treatment: 5 g of shungite were ground in a mortar to obtain a fine powder, sifted through double sieves, taking an average portion. We obtained particles of approximately the same size (from 0.25 to 1 mm). The powder was divided into two parts and placed in conical flasks of 250 mL. In the first method, the shungite was washed with water for several hours, periodically updating the distillate. After that, the solution was filtered into the flask through a funnel with a "white ribbon" filter. The filtrate was discarded. The processed shungite was saved for further work. In the second method, the shunigite powder was placed in a solution of 10 % hydrochloric acid. After 24 h of settling, the solution was filtered into the flask through a funnel with a filter paper. The filtrate was discarded. The processed shungite was saved for further work.

2.1.3 Synthesis of polymer-protected hydrogel with particles of activated shungite

In this work, an attempt was made to use hydrogels as a sorbent for cleaning water from heavy metal ions.
Starting material:

1) Acrylamide (AAM) -- ($CH_2CHC(O)NH_2$), (chemically pure, from Aldrich Chemical Co, USA);
2) N, N-methylene-bis-acrylamide (MBAA) - ($C_7H_{10}N_2O_2$), (Reanal company, Hungary);
3) N, N, N', N' - tetramethylethylenediamine -($(CH_3)_2NCH_2CH_2N(CH_3)_2$), (Shaanxi Greenbo Biochem Co., Limited Manufacturer, Trading Company)
4) Altay ammonium persulfate ($(NH_4)_2S_2O_8$) was selected as the initiator (GOST 20478-75, 2020);
5) The Inert gas is N_2;
6) Shungite treated with hydrochloric acid.

In the reaction of free radical copolymerization of acrylamide with N,N'- methylene- bis-acrylamide, acrylamide has a monomer function, and N,N'- methylene- bis-acrylamide has a cross-link function. Polymerization is initiated by ammonium persulphate ($(NH_4)_2S_2O_8$), tetramethylethylenediamine is used as a catalyst. Porosity

and hardness of the gel are defined by the share of monomers in it and amount of N,N'- methylene- bis-acrylamide in relation to acrylamide (Baiburdov et al., 2014).
Schungite was treated by hydrochloric acid was ground in ball mill to a size of < 45 μm. The resulting powder was stirred in water until a homogeneous suspension was formed. To receive a hydrogel sample, 71 mg of acrylamide and 20 mg of methylene-bis-acrylamide were dissolved in 4 mL of the suspension, then 10 mg of ammonium persulfate were added into this mixture. The reaction mixture was purged with nitrogen for 5 min for removing dissolved oxygen and 1 drop of N, N, N', N' - tetrametiletilendiamina was added. The monolithic samples were formed from the polymerization reaction and washed with distilled water to remove sol fractions. Then the washed samples were dried under vacuum to constant weight.

2.2 Sorption experiments

Sorption processes were studied using model solutions to determine the optimal contact time of the sorbent with the solution, and then wastewater samples were examined. The concentration of model metal solutions was 0.5 mg/L. Treatment of the studied solutions was carried out under static conditions. The sorbent consumption was 1 g of sorbent per 100 mL of the model solution. The method of experiments consisted in mixing model solutions with a certain suspension of various sorbents for 15 to 120 min in a static mode. Then the mixture was filtered through a filter with a "white ribbon".
The process was monitored by changing the content of metal ions in the solution. An atomic absorption analysis method was used to determine the concentration of metal ions. The determination of the ion content in wastewater and industrial water in this study was made in accordance with ST RK ISO 17294-2-2006. Water quality. Application of inductively coupled plasma mass spectrometry (ISP-MS) Part 2: Determination of 62 elements using an inductively coupled plasma mass spectrometer ICP-MSAgilent 5700 cx manufactured by AgilentTechnologies (USA).
After conducting experimental studies under static conditions, the degree of metal ions recovery was calculated based on the found residual concentrations of zinc and copper ions in solutions. The degree of metal ions sorption was calculated using Eq(1):

$$\alpha = ((C_0 - C) \cdot 100\ \%)) / C_0 \qquad (1)$$

where, C_0 - is the initial concentration of metals, mg/L; C - equilibrium concentration of metals, mg/L. The concentration of each metal ion (Zn^{2+}, Cu^{2+}) in the model solution was 0.5 mg/L.

2.3 Method of sorbent microstructure research

The phase composition of natural and synthetic sorbents was studied using electron-microscopic analysis methods. The microstructure of the samples was studied using the JEOL JSM 6000 scanning electron microscope, which combines the properties of a scanning and optical microscope.

3. Experimental part

3.1 Study of metal ions sorption by various sorbents in model solutions

Based on the results of experimental data, dependence diagrams of copper and zinc ions sorption degree on the contact time of model solution with sorbents were constructed (Figure 1).

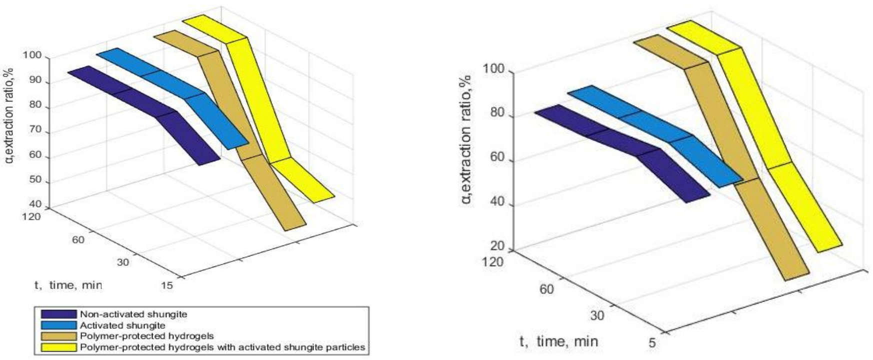

Figure 1: Dependence diagrams of the degree of copper and zinc ions extraction on the contact time of the model solution with sorbents

If compared, polymer protected hydrogel with activated shungite particles show good results of purification from copper and zinc ions.

3.2 Research of metal ions sorption process in real wastewater

The studies were carried out on real wastewater from the metallurgical plant of Ust-Kamenogorsk metallurgical complex "Kazzinc" at the initial concentrations (mg/L): Cu 0.013; Zn 0.183. The results of studies on real effluents are shown in Figure 2.

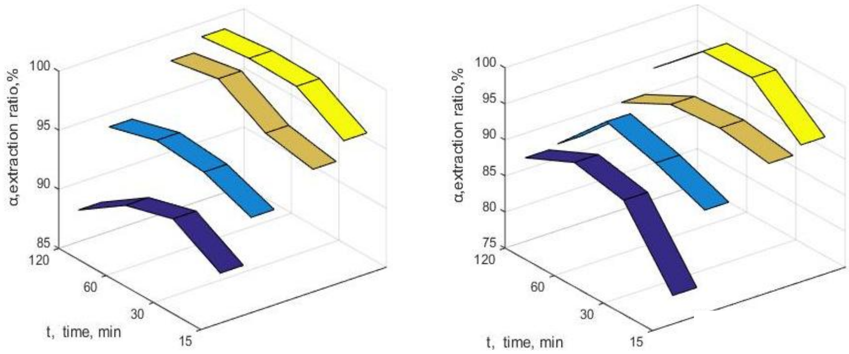

Figure 2: The dependence degree of copper and zinc ions extraction on the contact time of real effluents with sorbents

The dependencies of copper and zinc ions extraction degree on the residual concentration and contact time of the real effluents with polymer-protected hydrogel with activated shungite particles was also obtained (Figures 3 and 4).

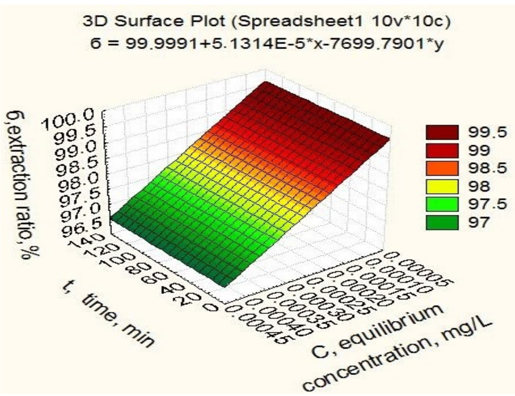

Figure 3: Diagram of the dependence of copper ions degree extraction on the contact time with the real runoff with polymer-protected hydrogel with activated shungite particles

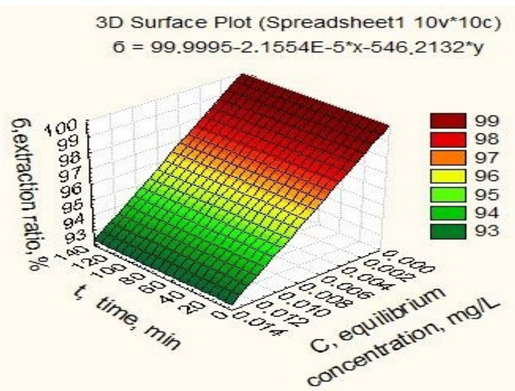

Figure 4: Diagram of the dependence of zinc ions degree extraction on the contact time with the real runoff with polymer-protected hydrogel with activated shungite particles

3.3 Study of waste sorbents structural features after wastewater treatment

During the experiment, the surface structure of natural and synthetic shungite was established. Electron microscopic images of shungite after wastewater treatment are in Figure 5.

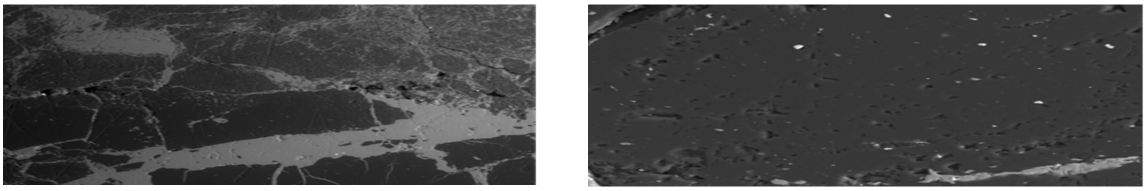

Figure 5: (a) Photos of the surface of natural shungite (b) Photos of a polymer-protected hydrogel with shungite particles

Figure 5a shows a General panorama of the shungite surface. As research has shown, the darkest parts in the photo are carbon. White inclusions in the form of bands and cracks of the mineral are silicon oxide. Shungite is a natural carbon, a mineral composition material, a carbonic substance that can form matrix, concentrate into big isolated clusters and form films on the crystals surface. It should be noted that there are numerous macroscopic quartz veins of irregular shape in massive shungite matrix, and they form cross-linked structure of the substrate here and there. It has been found out that shungite looks as different sized granules of different shape with rough surface formed by numerous pits of different diameter and depth. Supermolecular structure of shungite changes from globular to clustered, flake and film and results in clusters, layers, and hollow shells.

Figure 5b shows a polymer-protected hydrogel with activated shungite particles. The second image clearly shows the pores in the sample. Due to the different chemical composition of the samples, white inclusions in the form of stripes and cracks appeared on the sample surface. Polymer protected shungite is a homogeneous matrix surrounded by fine-grained shungite substance. Noticeable difference in carbon and silicon content can be connected both with primary divergence of rock composition and with secondary redistribution of a substance, in particular, quartz. Images of polymer protected shungite surface show that quartz is present in the form of light spherical primary grains; areas of dark colour are extremely concentrated with carbon and sharply depleted with silicon and oxygen that is due to quartz removal.

4. Results and discussion

The given work describes synthesis of bi-polymer material that is based on polymer-protected hydrogel with implemented phase (non-organic sorbent – particles of activated shungite). Introduction of shungite particles into polymer-protected hydrogel causes complicated physical and chemical processes that result in improvement of sorption properties. Improvement of polymer-protected sorbent physical and chemical properties is due to many factors and the most essential ones are the following: decrease of dead-weight ballast inclusions such as silicon, increase of material porosity due to hydrogel nature.

When micrographs of polymer-protected shungite surface were analysed it was found out that when shungite is introduced, structure of polymer surface sufficiently changes, shungite abundance increases integrity of material surface and contributes to uniform distribution of the components. This fact has favourable influence on interfacial adhesion of shungite and polymer, on formation of polymer structure and it causes improvement of physical-mechanical and sorption characteristics of polymer-protected shungite due to uniform distribution of shungite carbon in the polymer in the form of fine inclusions.

In the beginning of the research copper and zinc ions sorption was studied from model solutions with 0.5 mg/L metal ions concentration. It was found out that when natural sorbent (non-activated shungite) is used, copper (II) and zinc ions are extracted for 30 min up to 92.58 % and 84.1 % (Figure 1). Activated shungite increases extraction of copper up to 96.42 % and zinc up to 85.46 % for the same period of time. Polymer-protected hydrogel purifies model solutions from copper up to 97.20 %, from zinc 97.02 %, polymer-protected hydrogel with activated shungite particles provides the best results (Figure 1). So the degree of purification increases up to 98.96 % from copper ions, and up to 98.76 % from zinc ions (Figure 1).

The degree of copper ions extraction from real wastewater by non-activated shungite is 91.53 % (Figure 2). When activated shungite was used the degree of copper ions extraction increased up to 94.61 %. The use of polymer-protected hydrogel causes up to 98.46 % removal of Cu^{2+} ions from wastewater (Figure 2). High sorption activity to Cu^{2+} ions resulting in sorption degree increase up to 99.31 % was due to polymer-protected hydrogel with activated shungite particles (Figure 3).

Non-activated shungite provides 88.36 % purification of real wastewater from zinc ions (Figure 2). Activated shungite increases purification degree from zinc ions up to 92.07 % (Figure 2). Polymer-protected hydrogel causes 93.44 % purification of wastewater from Zn^{2+} ions (Figure 2). The use of polymer-protected hydrogel with activated shungite particles increases sorption activity to Zn^{2+} ions up to 99.34 %, providing achieving maximum permissible concentration rates (Figure 4).

5. Conclusions

The obtained dependence diagrams enabled the identification of the optimal time and to establish sorption equilibrium in the solution-sorbent system. To extract heavy metals ions (Zn^{2+}, Cu^{2+}) by natural sorbent (non-activated shungite), a necessary and sufficient condition is 30 min contact time of sorbent with the simulation solution, and 60 min contact time – with a polymer protected hydrogel with of activated shungite particles. Introduction of activated shungite particles into the structure of hydrogels that caused increase of sorption capacity of the obtained polymer-protected sorbent. It contributed to high degree of heavy metal ions extraction from real wastewater up to 99 %.

Further research will be devoted to the study of polymer-protected hydrogel with activated shungite particles reuse (after regeneration) for purification of metallurgical wastewater containing heavy metals ions. The synthetic sorbent will be reused, reducing the cost.

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