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The burnt solid in adsorption treatment of water from heavy metal ions

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Abstract. The process of adsorption of ions of heavy metals Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} from aqueous solutions with the mineral adsorbent burnt solid was investigated. Kinetic data on the adsorption process were obtained. Parameters of adsorption equilibrium using the Langmuir and Dubinin–Radushkevich equations have been calculated. The efficiency of extracting heavy metal ions upon modification of the adsorbent and in the area of low concentrations is shown.

1. Introduction

Development of the industrial sector makes it necessary to solve the problems of industrial wastewater treatment and waste disposal. The deteriorating environmental situation forces to tighten the requirements for waste dumping and wastewater treatment in business and public enterprises. Discharge of wastewater containing petroleum products, phenols, nitrogen compounds and heavy metals, as well as surfactants and other toxic compounds into the sources of centralized water supply exacerbates the situation with quality water supply. In the Kemerovo region, the chemical composition of the Tom River is formed under the influence of pollutants from wastewater from the enterprises of metallurgy, coke chemistry, as well as the coal and fuel and energy industries, agricultural enterprises and transport, and additionally through natural processes. The main pollutants of water bodies are still petroleum products, phenols, and heavy metal salts. Surface and underground waters are most intensively polluted with heavy metals in the areas of large-scale coal mining and metallurgical enterprises in the cities of Novokuznetsk, Leninsk-Kuznetsky, Belovo, Prokopyevsk, Kiselevsk, and Yurga. Heavy metal compounds form a group of toxicants. High toxicity, an ability to accumulate in human body, exerting harmful effects even in relatively small concentrations, determine the anthropogenic impact on the environment and on people.

Much attention is paid to the study of sorption purification of aqueous media from heavy metal ions using porous materials. Adsorption purification is more efficiently used as an additional purification after effluent treatment with chemical reagents by precipitating agents. Mineral adsorbents of natural origin are also very promising [1, 2]. The developed specific surface area and high absorption capacity with respect to liquids and solutes are characteristic of porous materials. They can serve as excellent carriers for fixing on the surface of various compounds when modifying them. Interest in modified mineral sorbents is caused by their specific properties: an inorganic carrier gives a sorbent such properties as high equilibrium rate, chemical resistance to aggressive media, mechanical strength; a modifier provides selectivity and completeness of ion binding [3]. The study focused on kinetics of adsorption processes allows one to determine the time required to achieve adsorption equilibrium and to obtain the parameters required for engineering calculations of these processes. The purpose of this paper is to study the process of adsorption of heavy metal ions on mineral adsorbents.

2. Materials and Methods

We used model solutions with variable content of heavy metal ions Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} as objects for our research. A mineral adsorbent is a burnt rock with a composition of 68.2% in SiO_2, 15.5% in Al_2O_3, which was obtained from the “Dalnie Gory” deposit in the city of Kiselevsk, Kemerovo region. It was formed as a result of thermal processes caused by the self-ignition of coal waste heaps in the worked-out spaces and waste dumps. After burning out an organic part in the rock, a mineral content increases up to 84.6%. The burnt rock of various fractions with a grain size of 1.5 mm, a grain shape factor of 2.1, and a porosity of 52–60% is used. It is modified with a sodium hydroxide solution with pH=12 and temperature of 60 °C.

Our research on kinetics of ion adsorption was carried out at the temperature of 25 °C on unmodified and modified with alkali (pH = 12) samples of adsorbents. Determining the equilibrium concentration of copper, cadmium, zinc, and lead ions in solutions was carried out by the complexometric method using Trilon B. To determine the adsorbent pore volume, we used the pycnometric method (also known as the “molecular probe” method) [4, 5]. To study the adsorption of heavy metal ions under static conditions, we used model solutions of their salts with variable concentrations. We found the value of adsorption by calculating a difference of the equilibrium concentrations of metal ions in an aqueous solution before and after adsorption, taking into account the volume of this solution and the mass of adsorbent [6]. We calculated the degree of purification as the ratio of the amount of adsorbed metal ion to the amount of metal ion in the initial solution. The Langmuir and the Dubinin-Radushkevich equations were used for reaching an analytical description of adsorption isotherms and calculating the parameters of adsorption equilibrium.

3. Results

Based on the experimental data obtained, the kinetic curves of the adsorption of cadmium, zinc, copper, and lead ions on the unmodified adsorbent were constructed (Fig. 1). Adsorption equilibrium is established within 40 minutes.

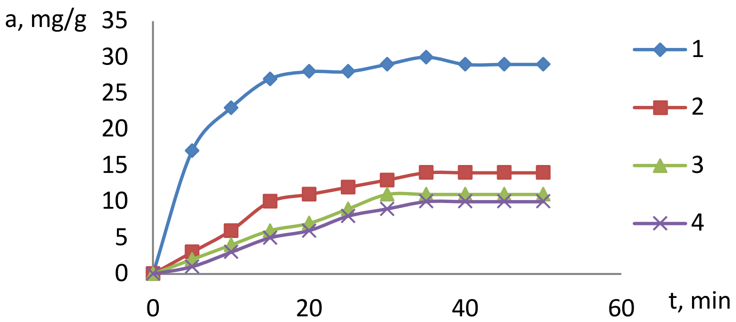

Figure 1. Kinetic curves of adsorption of metals ions Pb^{2+} (1), Cd^{2+} (2), Zn^{2+} (3), Cu^{2+} (4) from aqueous solutions on the burned rock (t=25°C).

The limiting adsorption capacity of the burned rock was Pb^{2+} 32.25 mg / g, Cd^{2+} 22.15 mg / g, Cu^{2+} 11.21 mg / g, Zn^{2+} 10.01 mg / g. To increase the number of surface adsorption centers, we processed the material under study with an alkali solution. Alkaline modification led to an increase in adsorption, the limiting adsorption capacity values of the treated burned rock were obtained at Pb^{2+} 46.08 mg / g, at Cd^{2+} 31.05 mg / g, at Cu^{2+} 18.32 mg / g, at Zn^{2+} 16.88 mg / g.

According to the research results of adsorption of heavy metal ions from aqueous solutions of natural and modified forms of adsorbents, adsorption isotherms were obtained, which are the main criterion for evaluating adsorption properties of the adsorbents under study and determining the dependence of adsorbent activity on concentration of adsorbate in equilibrium. Figure 2 shows the adsorption isotherm of lead ions.

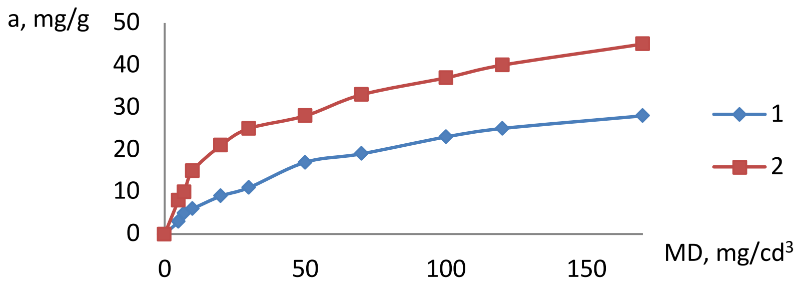

Figure 2. Adsorption isotherm of lead ions (II), samples of burnt rock without modification (1) and being modified (2).

Figure 3 shows the adsorption isotherms of lead ions in the coordinates of linear form (Langmuir equation).

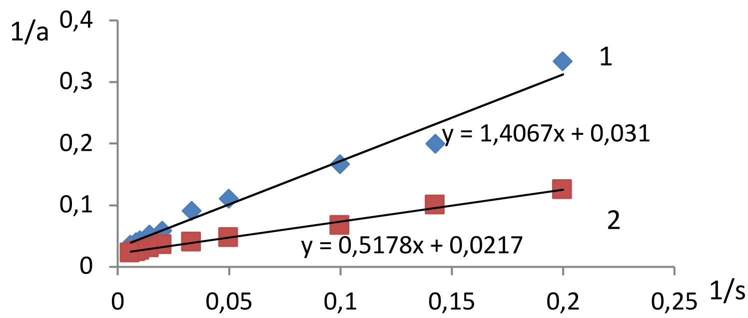

Figure 3. A linear view of the adsorption isotherms of lead ions (II), samples of burnt rock without modification (1) and being modified (2).

Based on the obtained experimental data, the parameters of adsorption of metal ions were determined (Table 1).

Table 1. Parameters of adsorption of heavy metals from aqueous solutions on the burned rock.

Ion / Adsorbent	Cleaning degree, %	Langmuir equation		Dubinin-Radushkevich equation		
		a_{max}, mg/g	К	a_{max}, mg/g	E, kJ / mol	W, cm^3/g
Pb^{2+} / burnt rock	49.5	32.25	0.031	32.6	1.31	0.036
Pb^{2+} / modified burned rock	87.5	46.08	0.021	45.5	2.03	0.050
Cd^{2+} / burnt rock	50.5	22.15	0.018	22.68	0.38	0.019
Cd^{2+} / modified burned rock	77.5	31.05	0.027	35.13	1.38	0.022
Cu^{2+} / burnt rock	55.5	11.21	0.091	11.62	0.81	0.011
Cu^{2+} / modified burned rock	84.0	18.32	0.121	19.05	2.79	0.016
Zn^{2+} / burnt rock	48.4	10.01	0.022	09.98	0.78	0.016
Zn^{2+} / modified burned rock	67.5	16.88	0.031	17.05	2.73	0.021

To determine the limiting stage of the diffusion process and establish the model of the samples' porous structure, the dependence of the degree of achieving the adsorption equilibrium (γ) and the dimensionless kinetic parameter (T) on the duration of mixing solutions (t) was studied. The equations determining the mass transfer coefficient and describing the external diffusion kinetics of absorption of solutes were used for calculations [7, 8]. The mass transfer coefficient (β) characterizes the adsorbate absorption rate by a unit volume of the adsorbent and is found according to the formula:

$$\beta_{\Pi} = \frac{dC}{dt \cdot (C_t - C_p)} \quad (1)$$

The value of T, proportional to the time of the process, is found according to the formula:

$$T=A\cdot\beta\cdot t \quad (2)$$

According to the linear dependence T = *f*(t), the adsorption of ions is limited by the process of external mass transfer for 5-10 minutes. Further deviation from the straight line shows that as the sorbent is developed, internal diffusion becomes a limiting stage in this hydrodynamic regime. More than that, values of the external diffusion mass transfer coefficients for the unmodified burnt rock were 0.004-0.008 min^{-1}, as well as 0.009-0.03 min^{-1} for the modified burnt rock.

Formation of a porous structure in the burnt rock took place as a result of an uncontrolled natural process. The volume of the adsorbent porous space falling on the micropores, determined by the "molecular probe" method, showed that micropores with a diameter of 0.35 nm make the greatest contribution to the porous space. The total volume of the porous space of the burned rock was 0.20 cm^3/g. The pore volume with a diameter of 0.35 nm was 38% of the total pore volume.

4. Discussion

The processing of adsorption isotherms of heavy metals according to the Dubinin-Radushkevich equation made it possible to calculate the following adsorption parameters of adsorbents: (a) a limiting value of the adsorption value in micropores; (b) a volume of the limiting adsorption space; (c) an energy value, which is the energy characteristic of the burning rock as a microporous adsorbent. It is known that low values of adsorption heat (up to 40 kJ / mol) and characteristic energy are typical for physical adsorption. For the studied adsorbents' samples, the value of the characteristic energy (E) is in the range of 0.38–2.8 kJ / mol, which indicates the physical nature of adsorption. The magnitude of the characteristic adsorption energy for modified adsorbents is 1.5–3.6 times higher than for unmodified ones, which indicates that, all other things being equal, the adsorption of heavy metals on modified adsorbents is more energy-efficient than on unmodified ones. Values of the limiting adsorption volume, calculated by the Dubinin-Radushkevich equation during the adsorption of heavy metal ions, are less than the total volume of micropores if being calculated by the "molecular probe" method. At the same time, incomplete filling of micropores with sizes of $0.35 < d < 0.67$ nm with heavy metal ions is observed. Thus, micropores with a size of less than 0.35 nm make the largest contribution to the adsorption of heavy metal ions (r = 0.091 - 0.133 nm).

Adsorption capacity of the modified adsorbent exceeds the capacity of the unmodified in 1.5-2 times. Therefore, we can assume that the extraction of heavy metals with a modified adsorbent occurs with the predominant participation of the donor groups of the modifier fixed on its surface and the silanol groups of the matrix.

For the practical use of adsorbents, in the process of water treatment, an important characteristic is the degree of extraction of the adsorptive. Studied adsorbents most effectively extract heavy metal ions in the area of low concentrations.

5. Conclusion

The obtained experimental data showed the possibility of using aluminosilicate mineral materials for the extraction of heavy metal ions from wastewater, the modification of which increases the degree of ion extraction. The obtained values of the degrees of purification of aqueous solutions with mineral adsorbents showed that the studied adsorbents most effectively extract heavy metal ions in the region of low concentrations. It is more efficient to use adsorption purification with the help of burnt rock as additional purification after treating effluents with chemical reagents with precipitating agents. Studies on the absorptive capacity of aluminosilicates of industrial origin, which are waste products of various industries, make it possible to search for directions of recycling industrial wastes that are not efficiently stored near enterprises and are harmful to the environment [9].

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