ADSORPTION OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS ON CARBON SORBENTS SELECTED FROM BROWN COAL

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ABSTRACT

Adsorption of heavy metal ions from aqueous solutions on initial, mechanochemically dispersed samples of humic acid, humine of Kara-Keche brown coal in the solid phase was studied.

A difference in the mechanism and type of adsorption of heavy metal ions on humic acid and humine was established. It is shown that in the series of studied natural carbon matrices, the initial sample of humine of Kara-Keche brown coal is the most effective sorbent of heavy metal ions from aqueous solutions.

Key words: Adsorption, heavy metal ions, humic acid, humine, brown coal.

INTRODUCTION.

The search for sorbents based on secondary sources of carbon raw materials is one of the priority tasks of rational nature management. In this connection, the objects of the present study are the initial and mechanochemically dispersed samples of humic acid, humine, selected from Kara-Keche brown coal. Dispersed samples of humic acid (GKd) and humine (GUd) were obtained by mechanochemical treatment of the initial samples of GK and GU in a ball mill. To avoid impurity of dispersed objects with metals, grinding balls and a glass of agate were used. Grinding was carried out at 300 rpm for 3 minutes. Technical characteristics of Kara-Keche brown coal, classification characteristics of humic acid, humine of Kara-Keche brown coal are given in articles [1,2]. The results of SEM, X-ray spectral microanalysis, IR spectroscopy of the investigated samples of carbon sorbents are presented in the works [3,4]. Specific surface areas of humic acid and humine, determined by both the methylene blue cation and ferricenium, are reported in [5].

The purpose of this study is a comparative characteristic of the adsorption of heavy metal ions from aqueous solutions on the initial, mechanochemically dispersed samples of humic acid, humine of Kara-Keche brown coal.

Experiment.
Determination of the compositions of aqueous solutions of chlorides of doubly charged metals, before and after adsorption, was carried out by complexometric titration. 5 ml aliquots of solutions of copper (II) and nickel (II) chlorides were selected, respectively, 0.5 ml of ammonia buffer and 0.0025 g of the murexide indicator were added. For the determination of cadmium cations, 2.5 ml aliquots of the cadmium (II) chloride solution were taken; 2 ml of ammonia buffer solution and 0.0025 g of black eryochrome indicator were added. In all cases, at the point of equivalence, the color of the solution becomes blue-violet. In calculating of the concentration of solutions of metals (II) chlorides, the following equation was used:

\[ C_1V_1 = C_2V_2 \]  

where \( C_1 \) is the determined concentration of metal (II) chloride solutions; \( C_2 \) – concentration of complexon III, 0.1 M; \( V_1 \) – volume of aliquot of MCl\(_2\); \( V_2 \) – complexon III volume spent on titration, ml.

The investigation of adsorption equilibrium was carried out as follows. To aqueous solutions of chlorides of doubly charged metals of a given concentration and a volume of 50 ml 0.1 g of adsorbent was added. The heterogeneous equilibrium in the aqueous electrolyte solution-adsorbent system was established for 24 hours in a dry-air thermostat at \( T = 298^\circ\text{K} \). At the same time, the first 2 hours the phases were mixed every 10 minutes. After the heterogeneous equilibrium was established, the aqueous solution of the metal (II) chlorides was separated from the adsorbent by means of a syringe filter with a pore size of 5 microns. The adsorption values were calculated by the equation:

\[ a = \frac{(c_e - c_p) \cdot V}{m} \times 1000 \] 

where \( a \) is the amount of adsorption (mmol / g), \( c_o \) and \( c_p \) are the initial and final (equilibrium) concentrations of adsorbate (mol / l); \( V \) – volume of solution, (l); \( m \) – mass of adsorbent, (g); 1000 – the transitive factor used to make the obtained data in mmol/g.

**Results and discussion.**

*Adsorption of ions of copper (II), nickel (II), cadmium (II) from aqueous solutions on initial, mechanochemically dispersed samples of humic acid of Kara-Keche brown coal.*

The experimental data of isothermal adsorption, pH of adsorbate solutions are presented in Fig 1.
Figure 1. Isotherms of heavy metal ions adsorption on samples of humic acid of Kara-Keche brown coal.

It is seen from Fig. 1 that the values of adsorption of heavy metal ions from aqueous solutions on mechanochemically dispersed samples of humic acid in all the cases considered are greater than in the initial samples. In this case, both for the initial and mechanochemically dispersed samples of humic acid, the adsorption values are arranged in a series, of the same type for the stability constants of acetate complexes of copper (II), nickel (II), cadmium (II) ions [6]. It can also be seen from the data in Fig. 1 that there is a significant decrease in the pH of water-electrolyte solutions after the adsorption of heavy metal ions, both in the initial and mechanochemically dispersed samples of humic acid. Along with this, the dependence of the adsorption values from the equilibrium concentrations of adsorbates in the coordinates of the Langmuir equation, presented in Fig. 2, is considered.
Figure 2. Adsorption of heavy metal ions on samples of humic acid of Kara-Keche brown coal in coordinates of Langmuir equation.

It is seen from Fig. 2 that linear dependences with high correlation coefficients are observed. In this connection, the parameters of the linear regression equations were used to calculate the limiting values of adsorption of heavy metal ions on the investigated humic acid samples that correspond to the condition of monomolecular adsorption from solutions on the surface of solid adsorbents. The totality of the obtained results allows to consider, that the adsorption of heavy metal ions from aqueous solutions, both on the initial and mechanochemically dispersed samples of humic acid of Kara-Keche brown coal, proceeds according to the ion-exchange mechanism of the Langmuir type, with the participation, in the main, of the surface adsorption centers of the carbon matrix of sorbents. Obviously, we are talking about ion-exchange processes involving, first of all, the carboxyl groups present on the surface of humic acid, which is confirmed by the results of the analysis of the surface morphology, IR-spectra of the research samples of carbon sorbents [3,4]. At the same time, the observed increase in the adsorption of heavy metal ions on a mechanochemically dispersed sample of humic acid in comparison with the initial one is explained by the greater availability of surface carboxyl groups to ion exchange of more
homogeneous in particle size and the content of the main elements mechanochemically dispersed sample of the sorbent [3,4].

**Adsorption of ions of copper (II), nickel (II), cadmium (II) from aqueous solutions on initial, mechanochemically dispersed samples of humine of Kara-Keche brown coal.**

The experimental data are presented in Fig 3.

![Figure 3](image)

**Figure 3.** Isotherms of heavy metal ions adsorption on samples of humine Kara-Keche brown coal

It is seen that the pH of water-electrolyte solutions after adsorption on humine sample varies insignificantly, and the adsorption of heavy metal ions on the initial humine is higher than on its mechanochemically dispersed sample. In this case, the adsorption values for both the initial and mechanochemically dispersed samples of humine are located in a lyotropic series, characteristic for the case of selective adsorption of charged particles on solid adsorbents [7].

It is noteworthy, that the linearization of the adsorption dependence on the equilibrium concentration of the adsorbate to determine the limiting values of adsorption is possible in the coordinates of the Dubinin-Radushkevich equation [8], as can be seen from Fig.4. Thus, unlike humic acid, on active centers of initial, mechanochemically dispersed samples of humine, located mainly in both the unevenness and in the pores of the carbon matrix of the sorbents, selective adsorption of heavy metal ions from aqueous solutions is realized.
It should be noted that the analysis of the experimental data in the coordinates of the Dubinin-Radushkevich equation can be applied in the case of volumetric filling of micropores of the carbon matrix of sorbents. It is obvious that the role of the pore structure of humine in the process of adsorption from solutions of heavy metal ions requires additional justification. In this connection, the task was to modify the initial sample of humine in such a way that the porosity of the new sample was significantly less than that of the mechanochemically dispersed humine of Kara-Keche brown coal. To solve this problem, the technology of thermal vacuum spraying of humine of Kara-Keche brown coal to a thin layer on a neutral substrate was applied [9].

Spraying of the initial sample of humine on a glass substrate was carried out with the help of the universal vacuum post VUP-4M at a temperature of 403-413 °K. The time of spraying was 8-10 sec. With the help of the transmission electron microscope TESLA BS-500, images of diffraction of initial and sprayed into a thin layer patterns of humine of Kara-Keche brown coal were shown in Fig. 5.

**Figure 4.** Adsorption of heavy metal ions on samples of humine of Kara-Keche brown coal in coordinates of the Dubinin-Radushkevich equation.

<table>
<thead>
<tr>
<th>ion</th>
<th>sorbent</th>
<th>The linear regression equation</th>
<th>$k_{corr}$</th>
<th>$n_{\infty}$ (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>GU</td>
<td>$\ln a = 1,28 + 0,28 \cdot \ln(C_p/3,17)$</td>
<td>0,99</td>
<td>3,50</td>
</tr>
<tr>
<td></td>
<td>G Ud</td>
<td>$\ln a = 1,02 + 0,24 \cdot \ln(C_p/3,17)$</td>
<td>0,99</td>
<td>2,77</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>GU</td>
<td>$\ln a = 1,16 + 0,28 \cdot \ln(C_p/3,06)$</td>
<td>0,97</td>
<td>3,19</td>
</tr>
<tr>
<td></td>
<td>G Ud</td>
<td>$\ln a = 0,67 + 0,18 \cdot \ln(C_p/3,06)$</td>
<td>1,00</td>
<td>1,95</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>GU</td>
<td>$\ln a = 1,32 + 0,22 \cdot \ln(C_p/2,98)$</td>
<td>0,99</td>
<td>3,74</td>
</tr>
<tr>
<td></td>
<td>G Ud</td>
<td>$\ln a = 1,13 + 0,26 \cdot \ln(C_p/2,98)$</td>
<td>1,00</td>
<td>3,10</td>
</tr>
</tbody>
</table>
Analysis of the photographs shows that the mineral components are present in both thin-layered and initial samples of the sorbent's carbon matrix. When carrying out adsorption of ions in a thin layer of humine, a glass substrate 4 cm$^2$ in area with a sprayed carbon sorbent dropped into the solution. The humine mass in a thin layer was established by the difference in the weights of the glass substrate before and after the spraying of the samples. Further, according to the above described method, the adsorption equilibria were investigated. The results of the experiments showed, that the concentrations of heavy metal ions in aqueous solutions before and after adsorption on thin-layer humine have practically not changed. Consequently, it can be concluded that the loss of porousness in thin-layer humine leads to a loss of its ability to adsorb heavy metal ions from aqueous solutions. Obviously, the obtained result indicates the significant role of the pore structure of humine of Kara-Keche brown coal in the adsorption of heavy metal ions from aqueous solutions.

A comparative characteristic of the adsorption of heavy metal ions from aqueous solutions on initial, mechanochemically dispersed samples of humic acid, humine of Kara-Keche brown coal. The limiting values of adsorption of heavy metal ions from aqueous solutions on humic acid and humine, respectively, characterize the adsorption capacity of the investigated carbon matrices. It is of practical interest to compare these values with each other to determine the most effective adsorbent of heavy metal ions from the number of samples studied. The results of the review are presented in the form of histograms in Fig. 6.
Figure 6. Comparative characteristic of adsorption ions of heavy metals on samples of humic acid, humine of Kara-Keche brown coal.

It can be seen from the histogram that the adsorption capacity of heavy metal ions for the investigated samples of humic acid and humine of Kara-Keche brown coal increases according to the series: $\text{GK} < \text{GKd} < \text{G Ud} < \text{GU}$.

Thus, based on the study, it can be concluded that the initial sample of humine of Kara-Keche brown coal, in the series of carbon matrices studied, is the most effective adsorbent of heavy metal ions from aqueous solutions.

REFERENCES.