

EXTRACTION, CHARACTERIZATION AND ADSORPTION PROPERTIES IN ASH OF COAL KARA-KECHE

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Isothermal adsorption of cationic and anionic dyes and ions of heavy metals on the ash of Kara-Keche coal and mechanochemically dispersed Kara-Keche coal has been researched. It is concluded the selective adsorption of organic and inorganic ions from aqueous solutions on the surface of the adsorbents. Comparative characteristic of the specific areas of surface of the ash of Kara-Keche coal and mechanochemically dispersed Kara-Keche coal has been shown.

Keywords: adsorption, ash, coal, methylene blue, methyl orange, lyotropic raw, ions of heavy metals, specific surface area.

Introduction

The use of thermal power plants waste has great economic and environmental significance. Large areas are required for the slag dumping annually [1]. In this connection necessity of the ash disposal emerges. Among the main areas of use of ash are the following: production of rare metal concentrates, such as Ge, Ga, Sc, Re, production of some types of alloys such as ferrosilicon, silumin, ferroaluminosilicon, production of alumina, aluminum sulfate or chloride; production of building materials (cement, bricks, stone molding, penozol et al.); calcification of acid soils [2].

According to the literature [1], the ash composition is close to the inorganic cation exchangers - zeolites having the formula $n\text{Na}_2\text{O} \cdot m\text{SiO}_2 \cdot k\text{Al}_2\text{O}_3$. The inorganic ash components form complex structures. Chemical and energy heterogeneity of these structures causes the ambiguity of their acid-base and sorption properties. Thus, unburned coal particles of ash are the active adsorbents of organic weakly dissociated substances. Due to these properties, the ash can be used to clean of slightly polluted wastewater.

Characteristic of research subjects

- Kara-Keche coal (sample of 2014 year) from the main reservoir deposits. Technical characteristics of brown coal Kara-

Keche is given in [3]. The test sample was a black coal dust, making by mechanochemical dispergation of fuel in a ball mill for one minute and following sieving on sieves with cell dimensions 60 mesh.

- Ash from Kara-Keche coal is a light powder produced by combustion of mechanochemically dispersed Kara-Keche coal in a muffle furnace. For this coal dust is applied a thin layer on a quartz substrate and was laid in a muffle furnace. Temperature of the furnace was gradually raised to 900 °C for 80 min. Coal was burnt at that temperature for one hour. Then the muffle furnace for 80 min gradually converted into a zero mode of operation in which the furnace heating elements are disconnected. Ash cooled in a muffle furnace for 24 h, and then transferred to a closed glass container. Ash resulting sample was a powder having a particle size not greater than 60 mesh.

- Methylene blue chloride and sodium salt of methyl orange were used as organic markers adsorbates. Area occupied on the surface of the adsorbent by a cationic dye molecule is 0.69 nm², and an anionic dye molecule is 0.64 nm² [4]. Composition of aqueous solutions of adsorbates before and after adsorption was determined by spectrophotometric method. Optical density measurements were performed at a wavelength of 670 nm for aqueous solutions of methylene blue and 400 nm for aqueous solutions of methyl orange.

- Chlorides of nickel, cadmium and copper were used as an inorganic adsorbates. The equilibrium concentrations of the aqueous solutions of heavy metal ions were determined by titration with 0.1 N solution of Trilon B [5].

- IR - spectra of the studied samples of Kara-Keche coal and ash were recorded on IR – Fourier-spectrometer Varian with KBr tablets in a ratio of 1:300, in the range of frequencies from 450 to 4000 cm⁻¹ (Fig. 1).

Based on the comparison of the data from Fig. 1 with tabulated characteristic frequencies [6] various groups of atoms in a part of the test substances were determined. The results of the study are presented in Table 1.

It is seen the spectra of coal and ash are quite different. Valence vibrations of -C-H groups of aliphatic hydrocarbons, the valence vibrations of +NH₂, C≡N groups, the valence vibrations of C=O in carboxyl, carbonyl groups, valence vibrations of the double carbon bond (C=C), conjugated with C=O or aryl, valence vibrations of the aromatic ring, deformation vibrations of -OH groups in alcohols and carboxylic acids are absent in the ash.

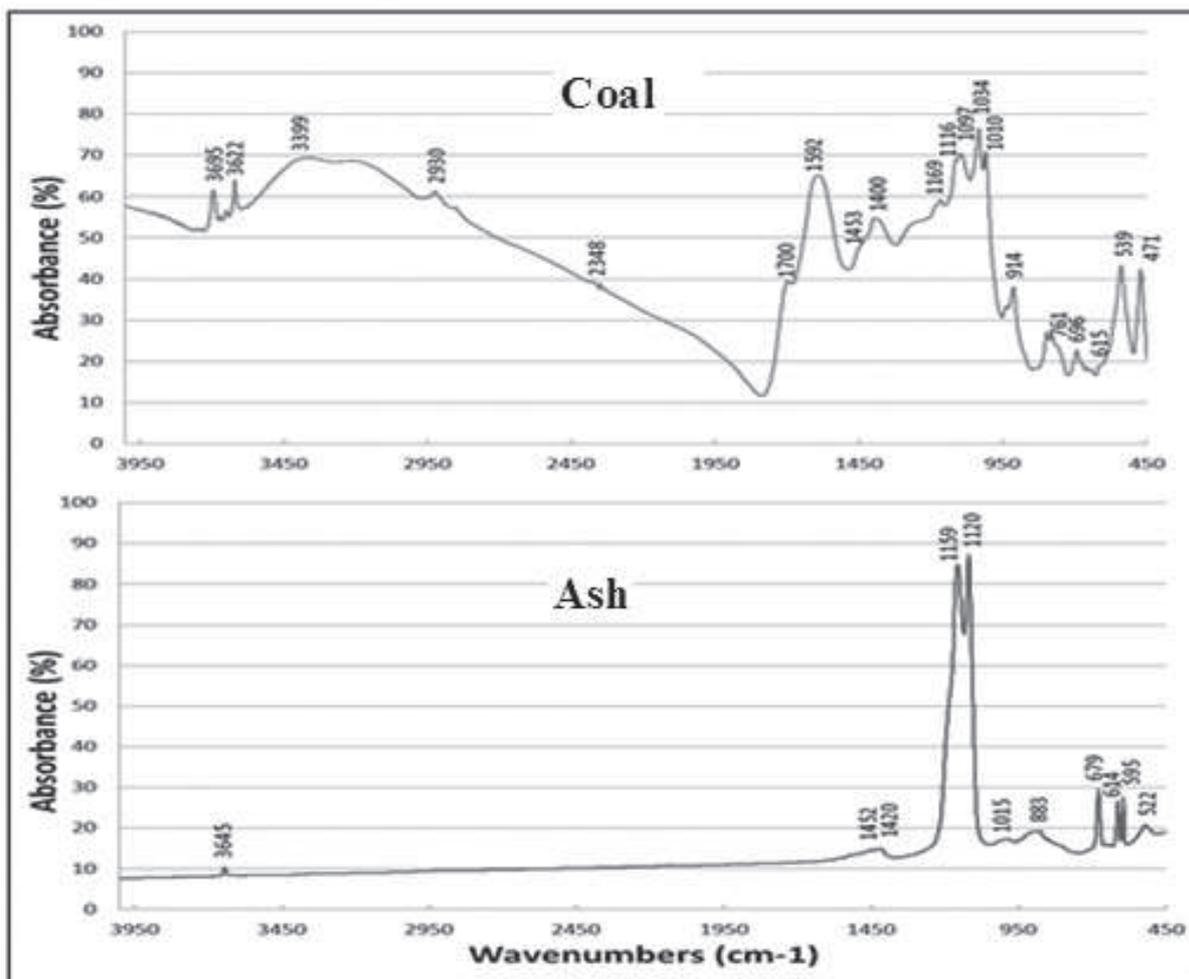


Fig. 1. IR-spectra of ash and Kara-Keche coal

Obviously, the result is associated with the loss of the carbon matrix in the ash from coal combustion in a muffle furnace.

Comparative analysis of the IR-spectra of Kara-Keche brown coal and ash shows almost complete coincidence of the characteristic absorption bands due to the presence of inorganic components in the studied adsorbents.

In both samples, there are peaks due to valence vibrations of OH groups in non-associated molecules, valence vibrations of carbonate CO_3^{2-} and hydrocarbonate HCO_3^- ions, valence vibrations of hydrosulfate HSO_4^- and sulfate SO_4^{2-} ions, valence vibrations of Si-O, deformation vibrations of Si-O, Si-O-Me groups.

Table 1

The characteristic absorption bands of ash and Kara-Keche coal

Groups	Absorption frequencies, cm ⁻¹	
	Coal	Ash
The valence vibrations of OH groups in the non-associated molecules	3622	3645
The valence vibrations of C-H aliphatic hydrocarbons	2930, 2859	- -
The valence vibrations of groups: ⁺ NH ₂ , C≡N	2348	-
The valence vibrations C=O in carboxyl, carbonyl groups	1700	-
The valence vibrations C=C, conjugated with C=O or Ar (aryl) The valence vibrations of the aromatic ring	1592	-
The valence vibrations of carbonate CO ₃ ²⁻ and hydrocarbonate HCO ₃ ⁻ ions	1453, 1400	1452, 1420
The valence vibrations of hydrosulfate HSO ₄ ⁻ and sulfate SO ₄ ²⁻ ions	1169, 1116	1159, 1120
Deformation vibrations of -OH groups in alcohols and carboxylic acids	1097	-
The valence vibrations of Si-O	1034, 1010, 914	1015, 883
Deformation vibrations of Si-O, Si-O-Me	761, 539, 471	679, 595, 522

Experiment and discussion of the results

Weight of 0.1g adsorbent was added to the 50 ml of aqueous solutions of organic and inorganic ions of predetermined concentration. Heterogeneous equilibrium in the system of the adsorbent - adsorbate aqueous solution was set for 24 h in a dry air thermostat at the T = 298 °K. The first 2 h phases were stirred every 10 min. After the establishment of equilibrium, aqueous solutions of electrolytes and dyes, accordingly were separated from the adsorbent particles on the syringe filter with 1-2 micron pore size.

Adsorption values were calculated by the formula [7]:

$$a = \frac{(c_0 - c_p)V}{m} 1000, \quad (1)$$

where C_0 , C_e – initial and equilibrium concentrations of adsorbate, (M); V – volume of the solution from which the adsorption occurs (L); m – mass of adsorbent (g); 1000 – conversion factor applied to the adsorption expressed in mmol/g.

Comparative characteristics of specific surface areas of adsorbents

In accordance with the method of adsorption from solutions on solid adsorbents an array of primary experimental data on adsorption of organic dyes on mechanochemically dispersed coal of Kara-Keche and ash was obtained (Fig. 2).

As seen from figure in the studied systems adsorption numerical values can be arranged in a row (I):

$$a_{Msu} > a_{MSz} > a_{Mou} > a_{MOz}. \quad (I)$$

Data of Fig. 2, row (I) show the adsorption of methylene blue on the mechanochemically dispersed coal Kara-Keche, and the ash from coal Kara-Keche increases with the increase of concentration of cationic dye. The same pattern occurs at adsorption of anionic dye (methyl orange) on the studied adsorbents. Note that adsorption of a cationic dye on mechanochemically dispersed coal Kara-Keche, and the ash from coal Kara-Keche is always greater than the orange anion. There is a slight decrease of adsorption of methylene blue and methyl orange on ash from Kara-Keche coal compared with mechanochemically dispersed Kara-Keche coal.

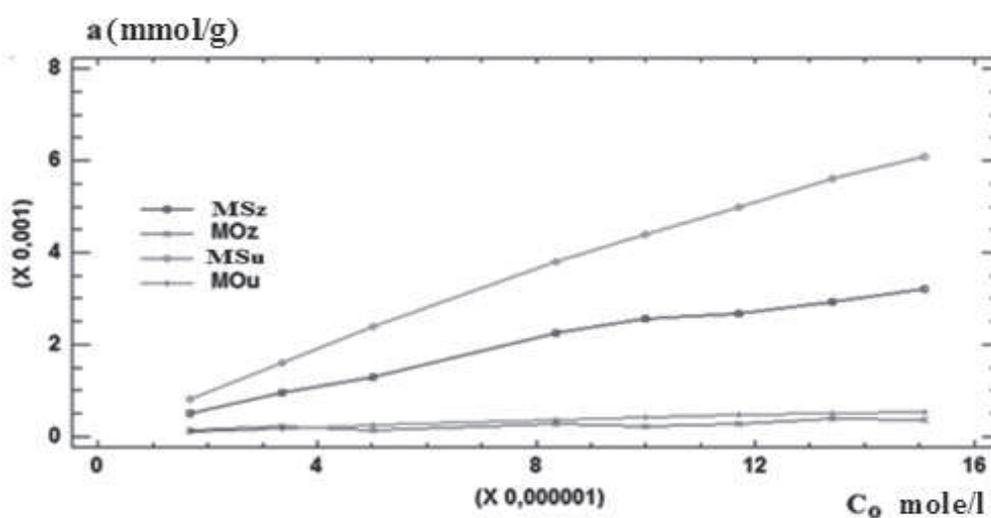


Fig.2. The adsorption isotherms of methylene blue (MS) and methyl orange (MO) on the ash (z) and Kara-Keche coal (u)

Obviously, this is due to the loss of carbon matrix in the ash, which is confirmed by the data of IR - spectra of samples. Thus, we can talk about the preferential contribution of inorganic components of ash and Kara-Keche coal in adsorption of cationic and anionic dyes, accordingly. However, due to the smallness of adsorption values not be expected the formation of strong chemical bonds of organic markers (organic salts) with inorganic components in the composition of adsorbents. In this regard, it can be assumed the physical adsorption of cationic and anionic dyes on the ash and Kara-Keche coal. In this case weak specific electrostatic interactions of adsorbent with an adsorbate provide a reversible binding of dyes on the centers of adsorption of inorganic nature of ash and Kara-Keche coal, respectively.

To set the type of adsorption, the data of Fig. 2 are considered in coordinates of Langmuir equation. The calculation results are shown in Fig. 3.

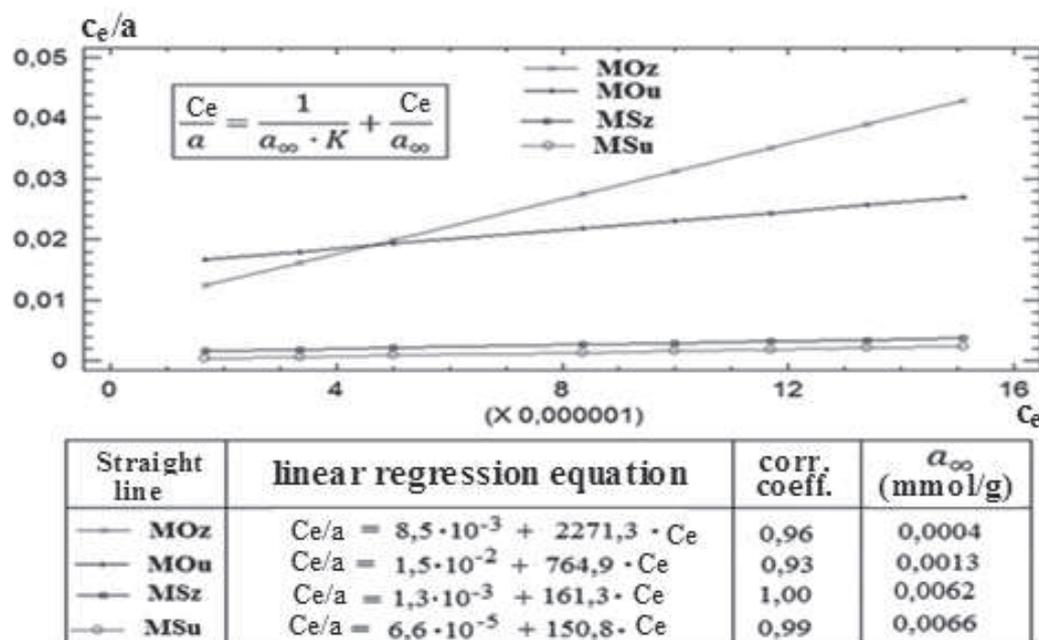


Fig. 3. Adsorption of methylene blue and methyl orange on the ash and Kara-Keche coal in coordinates of Langmuir equation

As seen from figure linear dependences of the high correlation coefficients are observed. This result allows us to consider the monomolecular adsorption of dyes on the surface of ash and Kara-Keche coal, respectively is mainly realized in the studied systems. Note the pH of aqueous solutions of methylene blue and methyl orange, before and after adsorption on the ash and Kara-Keche coal, accordingly didn't changed.

This fact excludes ion-exchange type of adsorption of methylene blue chloride and the sodium salt of the methyl orange on the ash and Kara-Keche coal accordingly.

Thus, the organic salts of cationic and anionic dyes most likely adsorbed from aqueous solutions on the ash and Kara-Keche coal respectively, by selective adsorption type.

Linear regression equations shown in Fig. 3, were used for the calculation of limit values of adsorption of methylene blue and methyl orange on the ash and mechanochemically dispersed Kara -Keche coal accordingly.

Note the limiting adsorptions are characteristics of the adsorption capacity of studied adsorbents [8]. For research systems this values can be arranged in the row (II):

$$a_{MSu}^{\infty} > a_{MSz}^{\infty} > a_{MOu}^{\infty} > a_{MOz}^{\infty} \quad (II)$$

As expected the rows (I) and (II) are the same. The maximum adsorption capacity is observed for mechanochemically dispersed coal Kara-Keche for adsorption of methylene blue and minimum adsorption of methyl orange for ash from Kara Keche. In turn, the values of limiting adsorption were used for the calculation of limit values of the specific surface areas of investigated adsorbents according to the equation (2) [8]:

$$S_{\infty}^{\text{lim}} = N_A \cdot a_{\infty} \cdot \omega, \quad (2),$$

N_A - Avogadro's number; a_{∞} - limiting adsorption; ω - the area occupied by a molecule of adsorbate.

The calculation results are presented in Fig. 4.

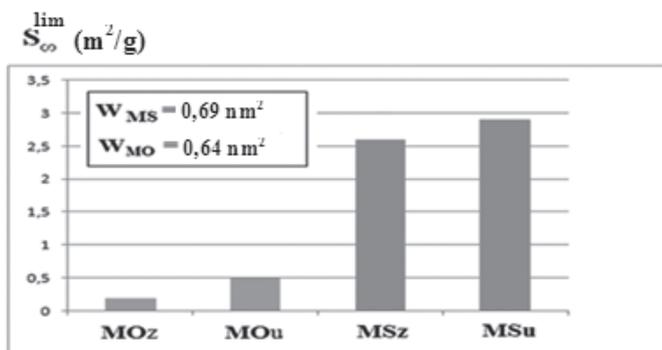


Fig. 4. Limit values for the specific surface area of adsorbents for methylene blue and methyl orange

The specific surface area of the adsorbent depends on the nature of the adsorbate. Thus, the adsorption method of determining the surface area of adsorbents assumes a deliberate choice of the corresponding marker (dye). Obviously, in this case, it is the methylene blue.

Adsorption of heavy metals ions on the ash of Kara-Keche coal

In previous studies, for example, in [9], the adsorption capacity of the components of the Kara-Keche coal as humic acid and huminto heavy metal ions was discussed.

In the present article the results of the adsorption capacity of the ash of Kara-Keche coal to ions of copper, nickel and cadmium are presented. In accordance with the method of adsorption from solutions on solid adsorbents an array of primary experimental data on adsorption of heavy metal ions on the ash of Kara-Keche coal has been obtained (Fig.5).

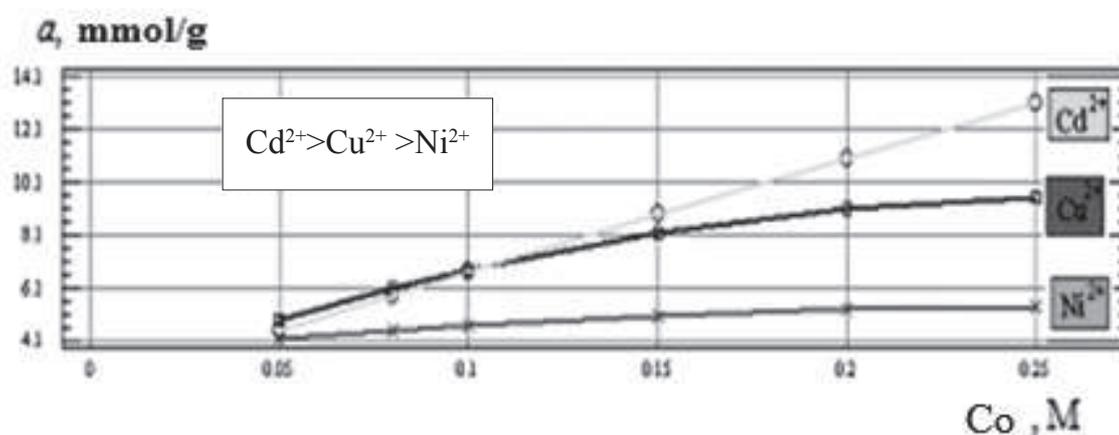


Fig. 5. Adsorption isotherms from aqueous solutions of chlorides of nickel, copper and cadmium on the ash of Kara-Keche coal determined at 298 K

As seen from Fig. 5 isotherms have a classic Langmuir character. It is known that in a row of similarly charged ions adsorption capacity depends on the degree of hydration and the radius [10].

According to our experiment, studied cations can be arranged in the following row on its adsorption capacity to ash of Kara-Keche coal:



Note that the row (III) for adsorption of studied ions on the ash of Keche-Kara coal, is in accordance with the lyotropicrows [7, 8]. In this

case, studied ions can be arranged according to crystallographic radius in the row: $r_{\text{Cd}^{2+}} > r_{\text{Cu}^{2+}} > r_{\text{Ni}^{2+}}$. Ions of cadmium and copper less hydrated, because they are large in size compared with nickel ions. This increases their adsorptive properties, because the hydrate shell weakens the electrostatic attraction [10].

Subsequently, in order to determine the adsorption capacity of ash of Kara-Keche coal and a constant of adsorption equilibrium, experimental data on adsorption of investigated electrolytes on the ash of Kara-Keche coal were treated in the coordinates of the Langmuir equation.

The results of the consideration are shown in Fig. 6.

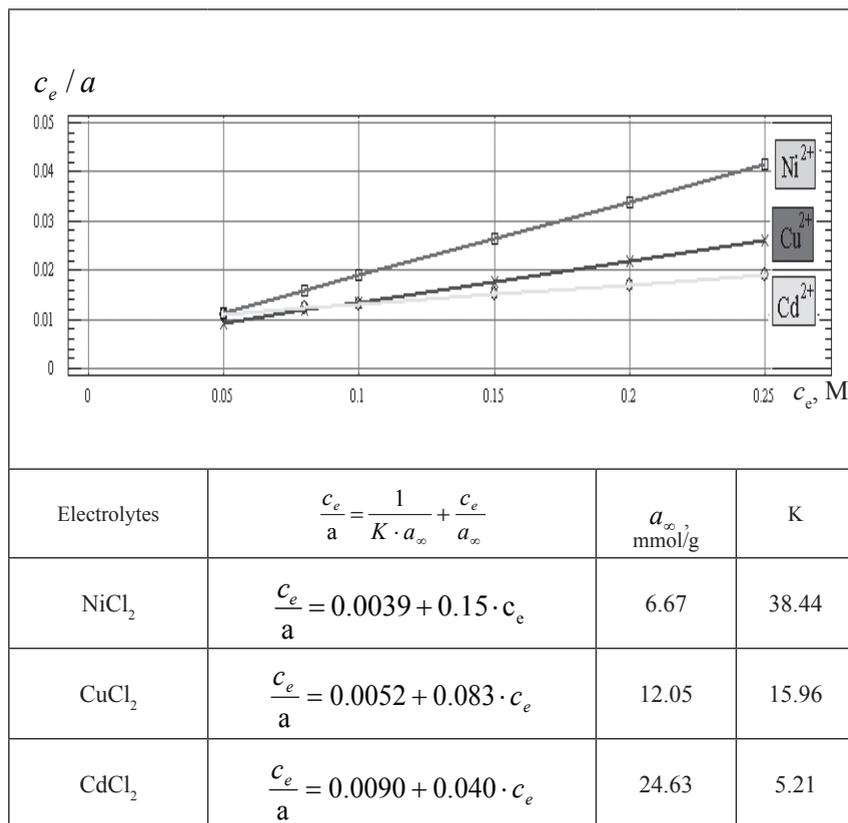


Fig. 6. Adsorption from aqueous solutions of chlorides of nickel, copper and admium on ash of Kara-Keche coal in the coordinates of Langmuir equation

Note that all dependencies are linear with high correlation coefficient. Taking into account the small magnitude of the adsorption equilibrium constants, it can be assumed that the adsorption of the ions on the ash of Kara-Keche coal is a physical. It can be explained by electrostatic attraction to the relevant negatively charged centers of the adsorption of the tested adsorbents.

To determine the mechanism of adsorption of studied two-charged ions on the ash of Kara-Keche coal pH of investigated electrolytes solutions was measured before and after adsorption. Measurements have shown a slight alkalization of test solutions of electrolytes after adsorption on ash of Kara-Keche coal. This is due to the properties of the ash.

In order to make conclusions about the mechanism of adsorption information about the physical and chemical properties, morphology of surface of Kara-Keche coal ash is required. Based on the available data we can assume a specific mechanism of adsorption of researched ions of heavy metals on the ash of Kara-Keche coal. For example, Cd^{2+} , Cu^{2+} , Ni^{2+} ions electrostatically fixed on the negative adsorption centers of the adsorbent and attract the counter ions, located in the liquid phase from the solution forming an electric double layer.

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