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Extraction of heavy metals from multicomponent solutions

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Abstract. The paper presents the results of studying the absorption of heavy metal ions from a multicomponent solution by coal mining waste. Acidic drainage solution was obtained by water leaching of technogenic sand of tungsten-molybdenum factory. It was found that manganese, zinc, copper and iron have high concentrations in the solution. Copper, iron and lead have a high affinity for the surface of coal. The usage of oxidized brown coal as an adsorbent can significantly reduce the concentration of heavy metals in multicomponent solutions despite their complex composition.

1. Introduction

Mining and processing of ore leads to the accumulation of waste that contains sulfide minerals. Tailings ponds are significant sources of acidic mine water, which are formed under the influence of oxygen, air, water and precipitation on rocks containing pyrite. Acid mine waters are characterized by low pH and high content of heavy metal ions. It can contaminate soil, surface water and groundwater, causing damage to all living organisms [1-8]. Heavy metals are toxic and not biodegradable [8, 9].

One of the many ways to combat pollution is the creation of artificial permeable barriers based on natural materials: carbonates, clay minerals, soils, apatites, zeolites, peat [10-12]. Oxidized low-quality coal can also be used as barriers, because they possess cation exchange ability due to the presence of humic substances having a multifunctional composition (mainly carboxyl and hydroxyl groups) [13-18].

The construction of the barrier is based on the study of sorption properties of the material [18-20]. Therefore, the purpose of this paper is to study the sorption of heavy metal ions by oxidized brown coal from a multicomponent solution.

2. Materials and Methods / experimental section

2.1. Technogenic Sands and oxidized brown coal

Technogenic Sands were used to prepare a multi-component drainage solution. Technogenic Sands were taken from tailings ponds of the Dzhydinsky tungsten-molybdenum factory, located in close proximity to the city of Zakamensk in Buryatia (Russia). One of the largest mining and processing complexes in Buryatia was built in 1934 and operated until 1997 [7]. The composition of Sands is represented by sulfide minerals (pyrite, chalcopyrite, Galena, sphalerite), hubnerite, wolframite, molybdenum. Therefore, acid mine waters contain significant concentrations of heavy metal ions that can migrate beyond the tailing dump and contaminate soils, groundwater and rivers [1, 4, 5].



Oxidized brown coal is a waste of the coal industry and a rich source of humic substances. Significant accumulations of oxidized coal are concentrated in the Trans-Baikal region. Coal samples for the study were selected from the most oxidized upper layers of the Gusinozersk coal Deposit. This Deposit is located 100 km from Ulan-Ude (the Republic of Buryatia, Russia). The content of humic acids was determined by leaching coal with a solution of sodium hydroxide (0.5 M) followed by precipitation from the alkaline humic extract with an aqueous solution of hydrochloric acid, drying the gel and weighing the dry matter.

Coal is a complex heterogeneous mixture of organic with lesser degree of inorganic substances. The chemical composition of the inorganic substance includes Si, Al, Fe, Ca, Mg, Ti, K, Na, S, P and trace elements which can be in various forms including carboxylates, chelated coordination compounds and discrete mineral phases.

In this paper, the technical characteristics of coal (moisture and ash content) were determined. Elemental analysis of coal samples was performed on the CNH analyzer (Karlo Erba 1106) by B C Batuev et al. [21]. The determination of total (carboxyl and hydroxyl) and carboxyl groups was carried out using barite and calcium acetate methods based on the interaction of acid groups of humic acids (COOH, ArOH) with Ba(OH)₂ or Ca(CH₃COO)₂. Unreacted excess of barium hydroxide or acetic acid was determined by titration. IR spectra were recorded on the Excalibur FTS 3000NX (Varian) IR spectrophotometer in the wave number range 4000-600 cm⁻¹.

Ash content of coal was determined in a muffle furnace at a temperature of 815 °C. Phase compositions of coal ash and technogenic sand were carried out by x-ray diffractometer D8 Advance (Bruker AXS, Cuka-radiation, detector VANTEC) in the range of diffraction angles from 10 to 60°. Chemical analysis of the samples was carried out using silicate analysis. Silicate analysis was carried out by preliminary decomposition of coal ash and sand, for this purpose, a mixture of sodium tetraborate and sodium carbonate in platinum crucibles at a high temperature (900 °C) was used. Then the molten mixture was dissolved in a hydrochloric acid solution. The content of silicon, aluminum, iron, titanium, calcium, magnesium, phosphorus was analyzed by photometric and atomic absorption methods. Photometric measurements of solutions were carried out on the spectrophotometer PE-5300VI (Russia). The sulfur content was determined by the Eschka Method. Coal samples were ground for sorption studies and different fractions were selected: 1 (5 ≥ d ≥ 3 mm); 2 (3 ≥ d ≥ 2 mm); 3 (2 ≥ d ≥ 1 mm) and 4 (0.5 ≥ d ≥ 0.25 mm).

2.2. Sorption experiments

Acidic drainage water (multicomponent solution) was prepared by leaching technogenic sand with distilled water at a mass ratio of sand/water = 1/2.5. Leaching was carried out in a vertical reaction column of quartz glass with a diameter of 22 mm and a height of 770 mm. The column was filled with sand (400 g), the height of the sand layer was 720 mm. Distilled water was poured into the column in small portions to evenly moistening of the sand. Water, seeping through the sand, dissolves the heavy metal compounds, then passes through the holes at the bottom of the column into the receiving flask. The total volume of water poured into the column was 1000 ml. The acidity of the resulting solution was measured with usage of the pH-meter with a combined glass electrode (Anion 4100). Electrodes were calibrated using buffer solutions. Then solutions were acidified with concentrated nitric acid for further analysis of the metal content.

Adsorption of heavy metal ions from drainage water was carried out at room temperature (20 °C) for different sorbent doses (1, 5, 10 and 20 g/L) and fractions of different sizes. The contact time was chosen on the basis of preliminary experiments, which showed that equilibrium had been reached within 2 h. Then the solutions were filtered and analyzed with the usage of the pH-meter and an atomic absorption spectrophotometer (AAS, Solaar M6) with an air-acetylene flame. Commercial standard samples of metal solutions with a concentration of 100 or 1000 µg/ml were used for the preparation of calibration solutions. Nitric acid was introduced to stabilize the calibration solutions. Working solutions were prepared by diluting a mother liquor to the required concentration interval.

Removal of metal ions (S , %) from the drainage solution was calculated from the difference between the initial and equilibrium concentrations using equation (1):

$$S = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the metal ion in the solution (mg/l).

Adsorbed amounts of heavy metal ions (mg/g) were calculated by the formula (2):

$$Q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where V is the solution volume (litres) and m is the mass of coal (g).

3. Results and discussion

3.1. Basic characteristics of the coal and technogenic sand

Some of the main characteristics of coal, including its elemental composition, moisture, ash content and concentration of carboxyl and phenolic hydroxyl groups, are presented in Table 1. The humic acid yield of coal (or 50-65% of the total mass of coal) was 70-90%.

Table 1. Proximate and elemental analysis of the oxidized brown coal (OBC).

Sample	Proximate analysis (wt.%)		Elemental analysis (wt.% dry basis)					Functional groups (mmol/g)	
	Ash	Moisture	C	H	N	S	O ^a	-(OH;COOH)	-COOH
OBC	22.0	9.0	67.1	3.1	1.3	0.5	28.0	6.2	2.0

^a Oxygen content was calculated by difference.

Oxidized coal is able to adsorb and bind heavy metal cations due to the presence of acidic functional groups.

In the IR-spectra of coal, weak vibrations are observed in the region of 600-800 cm⁻¹, which, apparently, belong to minerals. Absorption band at 1050-910 cm⁻¹ may belong to the silicates or certain phenoxy-structures (aromatic CCH in a single or condensed rings, or a substituted phenol and the hydrocarbon structure). The bands of carboxyl groups in the region ~ 1700 cm⁻¹ (oscillations of carbonyl groups C = O) and 1250 cm⁻¹ are very weak. Two bands at 1363 and 1575 cm⁻¹ refer to carboxylate anions. However, in this case, the band at 1575 cm⁻¹ is a consequence of the superposition of two bands: the skeleton oscillations of the C=C arenes and the carboxylate anion [22]. Thus, the carboxylic groups of coal exist mainly as carboxylates of calcium, magnesium, iron, etc.

Chemical analysis of ash shows that the main elements are Si, Al, Fe, Ca, Mg (Table 2). Also the ash contains a lot of sulfur, which does not evaporate from coal combustion as evidenced by the presence of anhydrite on the x-ray.

According to x-ray diffraction analysis, the main minerals in the coal ash are quartz, feldspar, anhydrite and hematite. Feldspar is mainly microcline. Quartz and microcline are the main minerals. Hematite and anhydrite are formed as a result of thermal transformations of the initial minerals pyrite, gypsum and calcite. Hematite is formed by oxidation of pyrite in the temperature range 100-500 °C. The main part of anhydrite is formed by dehydration of gypsum. It is possible that calcite and calcium, that are related to organic matter, interact with pyrite at 200-500 °C to form hematite and anhydrite [23].

Mineral substances of technogenic sand are characterized in this article [1]. The primary composition of the sand is quite diverse. The sulfide content is on average about 35%. This is mainly pyrite (55-59%), smaller proportion is sphalerite, galena, tetrahedrite, chalcopyrite present in amount of 0.1 to 5%. The high content of chalcopyrite and sphalerite in sulfide tailings leads to high concentrations of

copper and zinc in the drainage water from which the sulphates of these metals are formed. The main elements of technogenic sand are Si, Al, Fe, Ca, Mg and S (table 3). The composition of technogenic sand according to the X-ray analysis is represented by quartz, muscovite and sphalerite.

Table 2. Chemical composition of coal ash.

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	P ₂ O ₅
Composition (wt.%)	62.7	19.0	12.9	11.1	3.5	0.8	3.9	0.2

Table 3. Chemical composition of technogenic sand samples.

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	L.O.I. ^a
Composition (wt.%)	56.9	10.9	9.8	4.9	3.3	0.5	9.5	5.2

^a Loss on ignition.

3.2. Adsorption of metal ions by oxidized coal from drainage water

Distilled water extracts heavy metal ions from technogenic sand. Cu²⁺, Zn²⁺, Mn²⁺, Fe²⁺, Co²⁺, Pb²⁺, Ni²⁺, Cd²⁺ were found in the drainage solution. The acidity (pH) of the solution was 3.50 ± 0.05 . In the drainage solution Zn²⁺, Mn²⁺, Cu²⁺ and Fe²⁺ are the most concentrated (26.0, 34.0, 10.8 and 5.1 mg/l, respectively), and Ni²⁺, Co²⁺, Pb²⁺ and Cd²⁺ have low concentrations (1.60, 0.21, 0.84 and 0.37 mg/l, respectively). The acidity of the solution changed slightly and amounted to pH 4.0 ± 0.2 after sorption of metal ions. It is well known that pH is one of the controlling factors in sorption. In this paper, pH was measuring at the beginning and throughout the experiments. In all cases pH was between 3.5 and 4.0. This pH range is close to the optimum pH (4-5) for metal sorption by low rank coal (as some researchers report [6, 14, 19]), no pH adjustment was considered necessary.

The percentage removal of heavy metals by a sorbent with different particle sizes at different sorbent doses is shown in figure 1. The contact time of the sorbent with the aqueous phase was 2 hours. Removal of metal ions by coal is almost independent of the particle size. This is due to the fragility of the coal; the coal is easily destroyed in aqueous solution into small particles. The results of the study show that coal is better adsorb copper, iron and lead at a minimum dose of sorbent (1 g/L) from a multicomponent solution. This is probably a sign of greater affinity of Cu, Fe and Pb to the surface of oxidized coal. The adsorption of other metals increases gradually with increase of sorbent dose. This assumption is also confirmed by sorption isotherms (figures 2). Langmuir and Freundlich models (equations 3, 4) have been tested for compliance of experimental dependences Q and C using the method of nonlinear regression. This assumption is also confirmed by sorption isotherms (figure 2). The Langmuir and Freundlich models (equations 3, 4) were tested to fit experimental dependencies Q versus C using a method of non-linear regression. The equations which were used:

$$Q = \frac{Q_{max}bC_e}{1+bC_e} \text{ (Langmuir)} \quad (3)$$

$$Q = KC_e^{1/n} \text{ (Freundlich)} \quad (4)$$

where Q is the amount of metal ion adsorbed per unit mass of coal, C_e is the cation concentration at equilibrium, Q_{max} is the maximum adsorption capacity; K is related to the adsorption capacity and b, n are constants related to adsorption intensity.

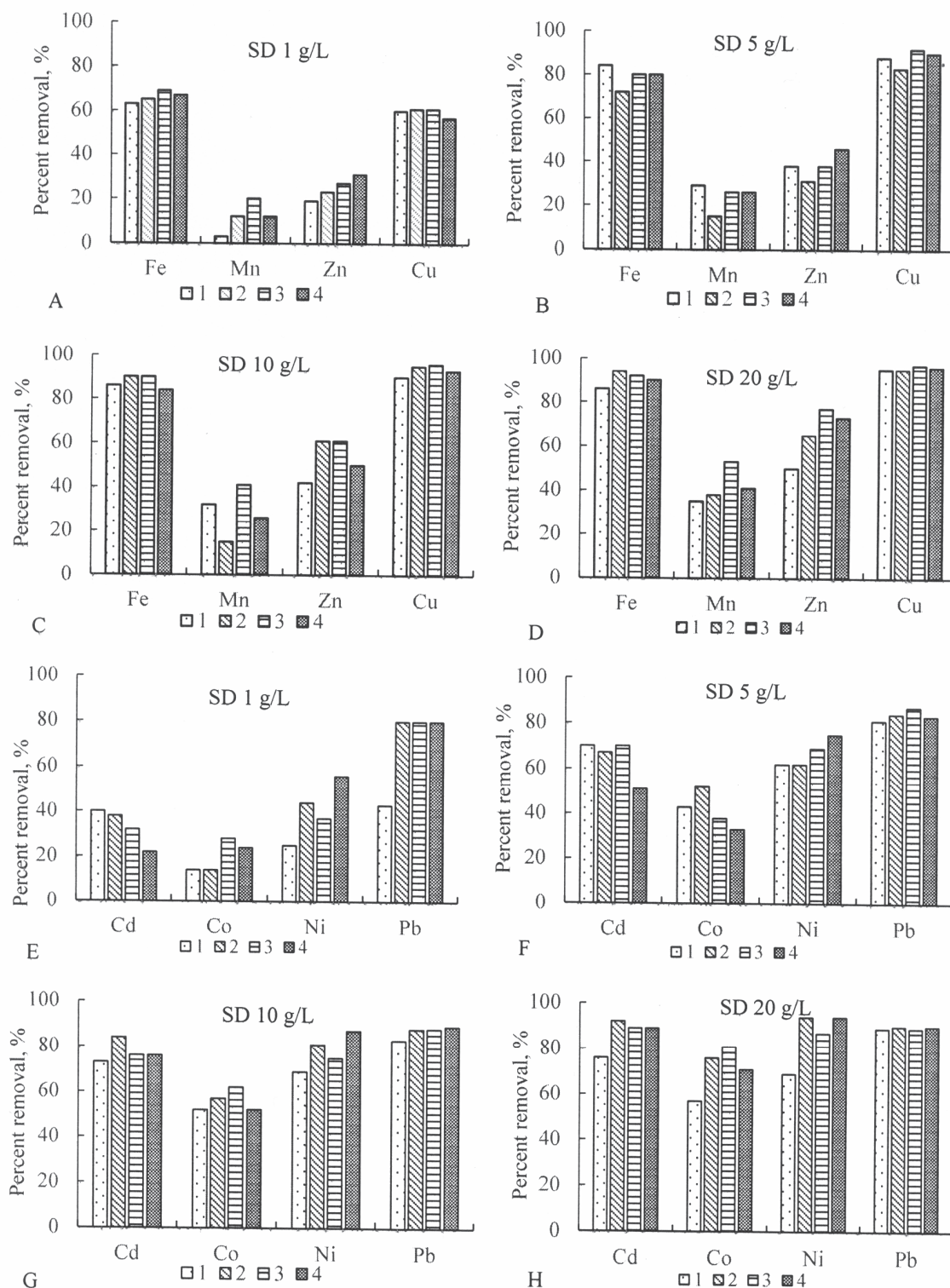


Figure 1. Percent removal of heavy metals for different fractions (1-4) at different sorbent doses (SD). Conditions: pH 3.5, temperature 20°C, contact time 2 h.

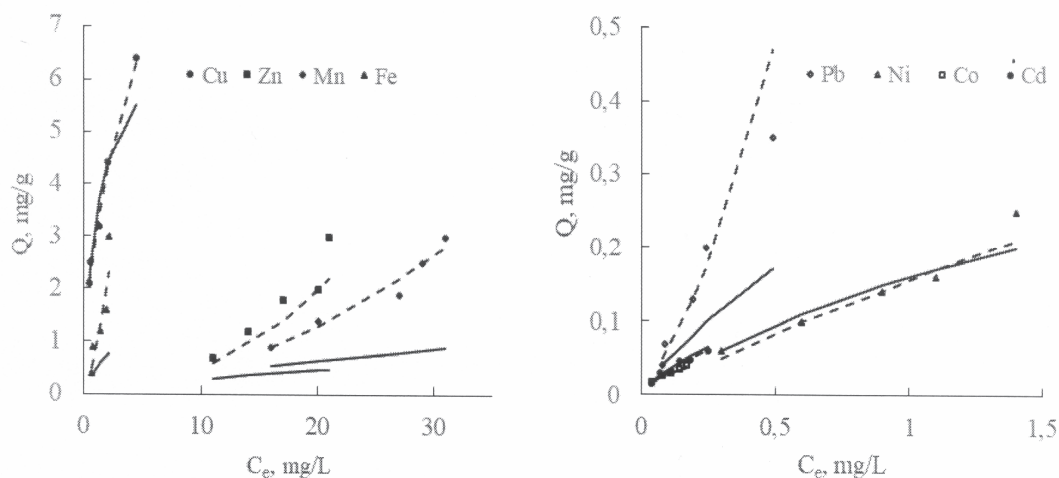


Figure 2. The heavy metal sorption isotherms by coal are established using the Langmuir model (solid line) and the Freundlich model (dotted line). Conditions: coal particle size $0.5 \geq d \geq 0.25$, pH 3.5, temperature 20°C , contact time 2 h.

The calculated parameters of the model are given in Table 4. As can be seen from the r^2 values in Figure 2, Freundlich model is better suited for most of the metals which was studied. Sorption capacities, which were estimated by Langmuir model, ranged from 0.06 mg/g for Co^{2+} to 6.9 mg/g for Cu^{2+} . Adsorption capacity in multicomponent experiments was reduced to $\text{Cu} > \text{Fe} > \text{Zn} > \text{Mn}$, this indicates competition for the available sorption sites. The order of sorption affinity of coal by mass and molar units is the same. Molar units of sorption capacity express the number of sorption centers occupied by sorbed atoms, regardless of their mass [19]. Copper has the greatest affinity to binding sites among metals with high concentration what is typical for humic materials [24].

Lead has a high affinity among low-concentration cations. Comparison of Pb, Ni, Co and Cd with Zn and Mn does not make sense because their concentrations are not comparable. The maximum adsorption capacity of coal, calculated by the sum of the Langmuir equation, is about 14 mg/g of the total sorption capacity. This is several times less in comparison with lignites [14, 18, 19]. However, the literature provides studies of the sorption of heavy metal ions by lignites from sufficiently concentrated solutions (from 100 to 1000 mg/L). Accordingly, the sorption capacity of these materials is higher than the capacity of the coals described in this article. Therefore, it is quite difficult to compare them.

Table 4. Parameters of the Langmuir and Freundlich isotherm for the sorption of metal ions onto coal.

Ion	Q_{\max} (mg/g)	b (L/mg)	r^2	K ($\text{mg}^{1-1/n}\text{L}^{1/n}\text{g}^{-1}$)	n	r^2
Cu^{2+}	6.90	0.870	0.96	3.030	2.00	0.99
Zn^{2+}	1.20	0.030	0.97	0.005	0.50	0.95
Fe^{2+}	2.30	0.250	0.78	0.840	0.72	0.84
Mn^{2+}	2.80	0.015	0.95	0.009	0.60	0.96
Pb^{2+}	0.49	1.110	0.89	0.850	0.89	0.95
Ni^{2+}	0.57	0.380	0.98	0.160	1.15	0.97
Co^{2+}	0.06	9.580	0.99	0.110	1.72	0.99
Cd^{2+}	0.14	3.450	0.98	0.160	1.47	0.96

Ion exchange is the most common way of metal sorption on coal. The metals listed above are adsorbed on the surface of the coal by binding to functional coal groups, predominantly carboxyl and to a lesser extent phenolic hydroxyl groups, as they dissociate at $\text{pH} \geq 8$. The IR spectra of coal shows that

carboxyl groups are mainly in the form of metal carboxylates (e.g. Ca^{2+} , Mg^{2+} , Na^+ , etc.). Consequently, the sorption of heavy metal ions from coal should release Ca^{2+} ions and other light metals (Al^{3+} , Fe^{2+} , K^+ , Mg^{2+} and Na^+) [6].

The usage of oxidized brown coal as an adsorbent can significantly reduce the concentration of heavy metals in multicomponent solutions, despite their complex composition. Concentrations of cadmium, cobalt and lead are less than 0.1, nickel is less than 0.2, iron and copper are less than 0.6 mg/L. Zinc concentration can be reduced to a few mg/L, and for manganese there is no significant decrease in concentration. The concentration of Mn decreases only 1.5 times, while all other metals reduce the concentration several times and even dozens of times.

The presented results show that coal is an effective sorbing material for removal of Cu, Fe, Pb, Ni from an acidic multicomponent solution.

4. Conclusion

In this paper, the sorption of heavy metal ions (Cu^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+}) on oxidized brown coal was studied. Acid drainage solutions were obtained by water leaching of technogenic sand of the Dzhydinsky tungsten-molybdenum factory. The sorbent showed the ability to adsorb metals with different efficiency. Copper, iron and lead have the greatest affinity to the surface of coal. Manganese has the lowest affinity for coal when it is adsorbed from an acidic solution. These findings indicate the high suitability of coal as an affordable, inexpensive and effective material for the removal of heavy metals from wastewater and acidic drainage waters. Consequently, coal can be used as a permeable reactive barrier to protect the environment in places where sulfide tailings are stored.

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