

CONCURRENT SORPTION OF COPPER AND CHROMIUM CATIONS BY NATURAL ZEOLITE

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Received: 13.02.2017

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Abstract. The aim of this work was to study the process of adsorption of Copper and Chromium cations by natural zeolites in static conditions. The change of the chemical composition of the surface of the zeolite as a result of sorption of heavy metals was investigated. The influence of the type of the ions and pH selectivity in absorption of heavy metals removal by zeolite was analysed. The reasons for the selective extraction of Copper from two-component solution were explained.

Key words: Copper, Chromium, heavy metals, adsorption, wastewater

1. Introduction

Heavy metals (Mercury, Lead, Cadmium, Zinc, Copper, Chromium, Arsenic) are part of the common and very toxic pollutants. They are widely used in various industrial enterprises, so despite the clean-up, the content of heavy metals in industrial waste water is rather high [1, 2]. Large masses of these compounds fall into the ocean. In areas polluted by industrial waters, their concentration in solution and suspensions was greatly increased [3, 4]. These are emissions from industrial and domestic effluents, smoke and dust from industrial plants, particularly electrolytic ones, exhaust gases of internal combustion engines. Since all heavy metals and toxic maximum permissible concentration averages about 0.1 mg/l, it is advisable to apply sorption methods for purification of waste water that will allow to remove trace amounts of impurities [5, 6, 7].

2. Experimental studies

For this study, samples of 3.93g of Copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 4.58 g of Chromium nitrate $\text{Cr}(\text{NO}_3)_3$ were put in a 1litter flask. Salts were

dissolved in distilled water. The content was mixed thoroughly until dissolved. The solution was adjusted to a volume of 1 litter. In the prepared solution the ratio of the mass amounts of Copper and Chromium ions amounted to 1: 1.

From the prepared solution 6 samples of volume: 2 ml, 10 ml, 20 ml, 40 ml, 80 ml and 120 ml, 160 ml, 200 ml were selected and put into 200 ml volumetric flasks. The content of each sample was filled with distilled water to the mark and a sample of 2 g of natural zeolite was put into the capacities.

The content of each sample was mixed and closed with lid for its infusion for three days in an incubator at a temperature of $20 \pm 0,5$ °C.

After three days the solution was filtered and zeolite was dried to constant weight.

The amount of absorbed Copper and Chromium ions was determined by use of the X-ray fluorescence analyzer "EXPERT 3L" [8, 9].

X-ray fluorescence analyzer is used to determine the mass fraction of elements with atomic number of 12 (magnesium) to 92 (uranium) in homogeneous monolithic samples. For qualitative analysis it is sufficient to use the X-ray spectrometer to determine the energy lines of the object and their values to identify the existing elements. Quantitative analysis is based on the assumption of proportionality between the intensity characteristic of the X-ray element and its content in the object under control.

3. Results and interpretation

The analysis of the quantity of heavy metals adsorbed by zeolite was carried out by use of X-ray fluorescence analyzer (Table 1). The elemental composition of the surface of the zeolite is shown in Fig. 1. and Fig. 2.

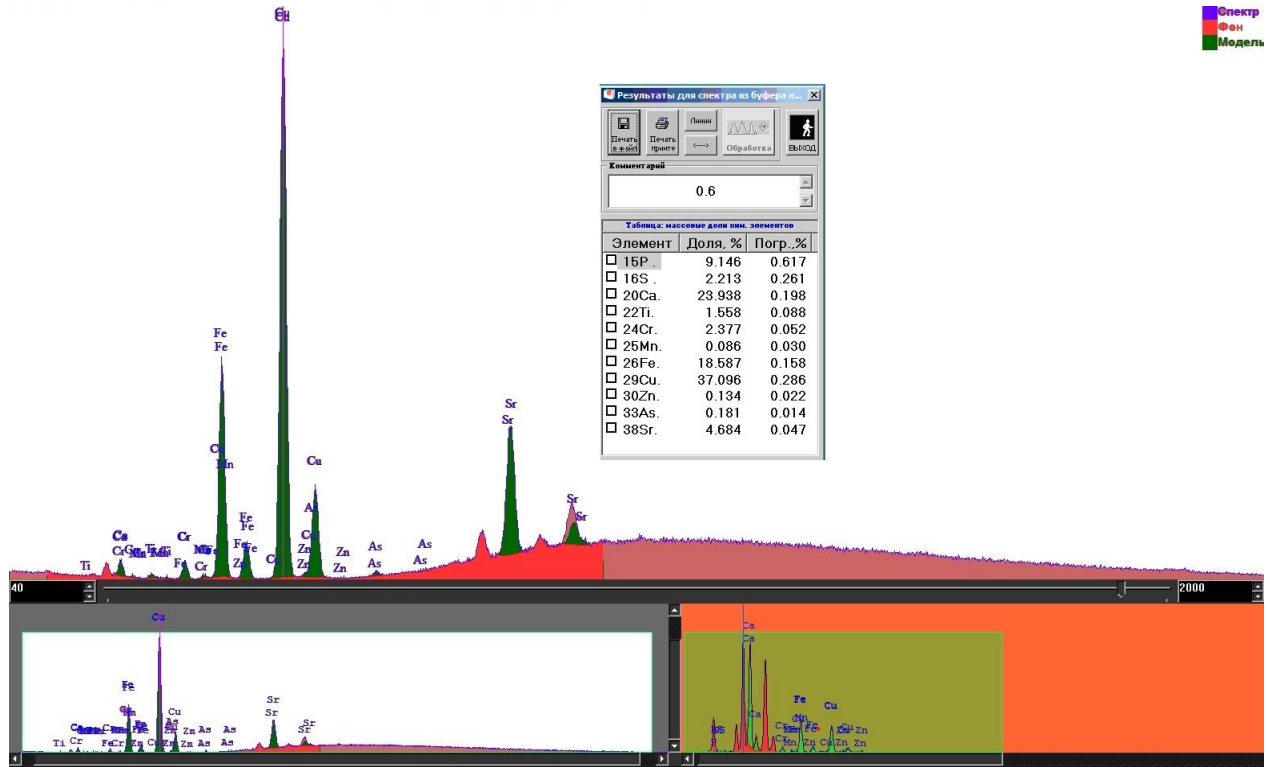


Fig. 1. Spectrum of zeolite surface after adsorption of Cr^{3+} and Cu^{2+} ions from the solution with the initial concentration of $C_{\text{initial}} = 0,6 \text{ kg/dm}^3$

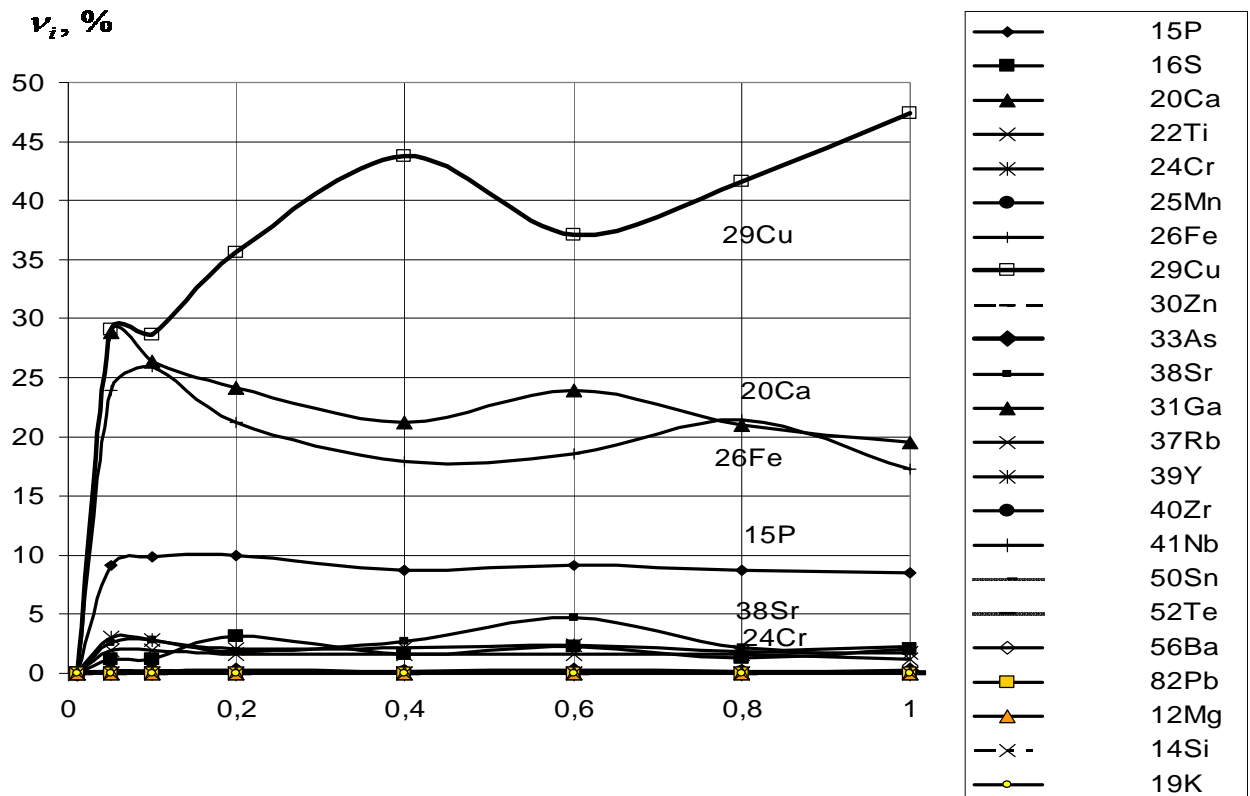


Fig. 2. Mass fraction of elements on the surface of the zeolite depending on the initial concentration of Cr^{3+} and Cu^{2+} ions in the solution

Table 1

Dependence of the amount of adsorbed cations of heavy metals by zeolite to its concentration in the initial solution

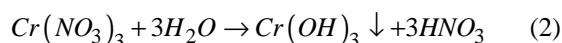
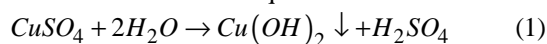
The concentration of ions in the initial solution. kg / dm ³	Quantity of adsorbed heavy metals. %	
	Copper (Cu)	Chromium (Cr)
0.01	0.628±0.019	0.459±0.016
0.05	29.026±0.159	2.966±0.061
0.1	28.631±0.158	2.740±0.046
0.2	35.591±0.383	2.047±0.051
0.4	43.728±0.360	2.123±0.048
0.6	37.096±0.286	2.377±0.052
0.8	41.604±0.181	1.840±0.040
1	47.380±0.255	1.679±0.036

Depending on the concentration of heavy metal ions in the solution, their concentration changes on the sorbent surface [8, 9]. Analyzing the experimental results, we see that Copper ions are absorbed by the sorbent much better compared to Chromium ions. Despite the lone concentration of Chromium and Copper ions, selective removal of Cu²⁺ occurs in the solution. As seen from the experimental results, the concentration of Copper on the surface of the sorbent increases from 0.628 % of the mass with concentration of 0.01 g/dm³ to 47.380 % of the mass with concentration of 1 g/dm³. The concentration of Chromium ions on the surface of the sorbent after adsorption was little dependent on increasing the concentration of Cr³⁺ in the initial solution.

Adsorption of ions on the sorbent surface that is in contact with the solution is caused by the electrostatic interaction, but it is not necessarily selective. There are several factors that affect the ability of the sorbent to adsorption of this particular type of ions [10]. The atomic radius of Copper is slightly larger than the Chrome R_{Cr} = 1.27Å, R_{Cu} = 1.28 Å. According to Goldschmidt and Pauling R_{Cr} = 0.35 ... 0.52 Å, R_{Cu} = 0.98 Å. According to Belov and Bokiy R_{Cr(3+)} = 0.64 Å, R_{Cu(2+)} = 0.8 Å [11]. So, despite the fact that the charge of Chromium ion is higher, it is obvious that the radius of the atom is crucial in the process of sorption. This supports better sorption of Copper compared with Chromium.

By the law of Paneth – Faience – Khan, if the solution contains two or more ions and other factors are identical, the ion which together with one of the ions of sorbent crystal lattice forms a compound with the lowest solubility, will be adsorbed first of all.

In this case, the solution contains the same concentration of ions of Copper and Chromium. Since these compounds are formed by strong acids and weak bases, the solution is hydrolysed. Acid and insoluble hydroxides of the corresponding metals are formed in accordance with the reaction equations:



According to datasheets, Copper hydroxide has a much lower solubility than Chromium hydroxide. Products of solubility of the formed compounds are presented in Table 2.

Table 2

Products of solubility of Cu(OH)₂ and Cr(OH)₃ depending on the acidity of the environment [8]

Compound	Solubility product SP	-lg(SP)
Cr(OH) ₃	4.0·10 ⁻¹⁵	14.4
Cu(OH) ₂	1·10 ⁻¹⁹	19.0

To display the phase composition of a two-component solution of heavy metals a chart has been built by use of the MEDUSA (Make Equilibrium Diagram Using Sophisticated Algorithms) and HYDRA (Hydrochemical Equilibrium Constant Database) software.

Analyzing the chart we can see that the solution in the pH range of 0-3 contains highly soluble complexes. With pH of 3.7, Cr₂O₃ is formed and in the pH range of 4-6, Copper hydrosulphates are formed, which are insoluble compounds.

If the solubility product of Cu(OH)₂, which is formed by the hydrolysis of (1) is equal to 1 · 10⁻¹⁹ [9], the concentration of Cu²⁺ in the initial solution at the beginning of the experiment is equal to 0.016 mol / dm³, then, pH on this early precipitation of Copper is equal:

$$[Cu^{2+}][OH^-]^2 = SP_{Cu(OH)_2} = 1 \cdot 10^{-19} \quad (1)$$

$$pH = 14 - pOH = 14 - \left(-\lg \sqrt{\frac{SP}{[Cu^{2+}]}} \right) =$$

$$= 14 - \left(-\lg \sqrt{\frac{1 \cdot 10^{-19}}{0.016}} \right) = 5,39$$

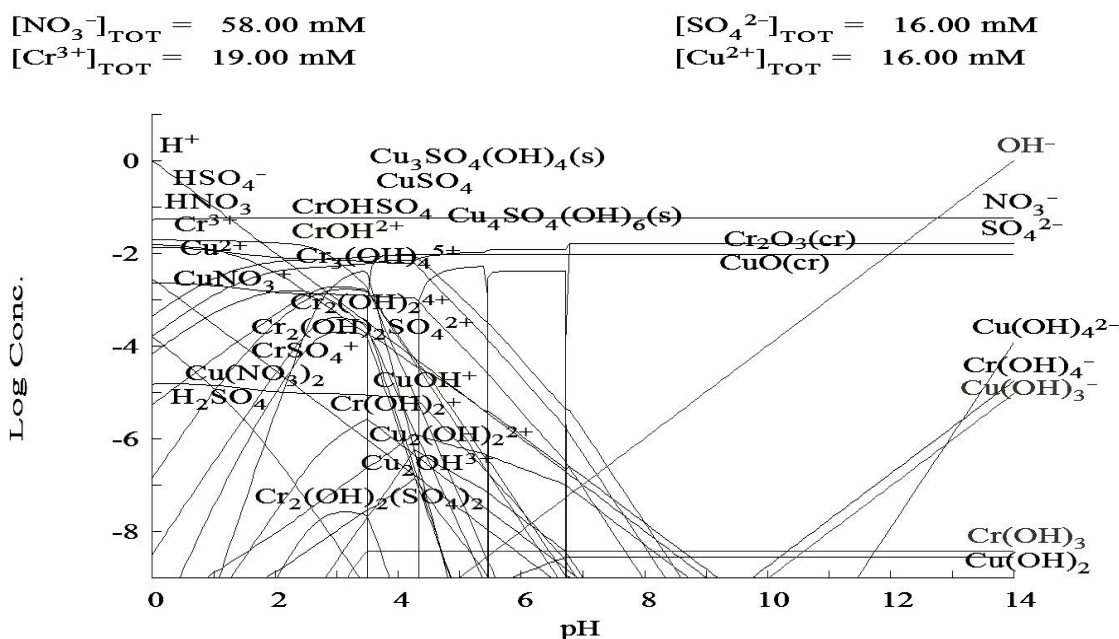


Fig. 3. Logarithmic chart of a two-component system, depending on the pH

If the solubility product of $\text{Cr}(\text{OH})_3$, which is formed by the hydrolysis of (2), equal to $4 \cdot 10^{-15}$ [9], the concentration of Cr^{3+} in the initial solution at the beginning of the experiment is equal to $0,019 \text{ mol} / \text{dm}^3$ then, the value of pH at this early precipitation of Chromium is equal:

$$[\text{Cr}^{3+}][\text{OH}^-]^3 = SP_{\text{Cr}(\text{OH})_3} = 4 \cdot 10^{-15} \quad (2)$$

$$\begin{aligned} \text{pH} = 14 - \text{pOH} &= 14 - \left(-\lg \sqrt[3]{\frac{SP}{[\text{Cr}^{3+}]}} \right) = \\ &= 14 - \left(-\lg \sqrt[3]{\frac{4 \cdot 10^{-15}}{0,019}} \right) = 9,77. \end{aligned}$$

According to the calculated data we can see that at fixed pH values Copper ion will settle faster than Chromium and according to the law of Paneth – Faience – Khan it will be adsorbed better, which was found experimentally.

Apparently this is the reason for the selective extraction of Copper from a two-component system. Also it is confirmed by the previous studies [6, 7].

During experimental studies the reduction of calcium, magnesium, iron and rare earth metals concentration on the surface of the sorbent was identified. This is due to the interaction of ion-exchange hydrogen ions and heavy metals from the test solutions with zeolite. As a result, these exchange cations move from the surface of the sorbent into the solution.

Conclusions

The elemental composition of the surface of the sorbent by X-ray fluorescence method after absorbing heavy metals from the binary system containing Cu^{2+}

and Cr^{3+} ions were studied. The mechanism of sorption extraction of Copper and Chromium ions from the solution was theoretically grounded. It was established that the selective extraction of metals is effected by the element radius and its hydroxides solubility. The conditions of the corresponding metals hydroxides precipitation were calculated and logarithmic chart of a two-component system depending on the pH was built.

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