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ADSORPTION OF Cu (II) and Cr (III) IONS FROM AQUEOUS MEDIUM IN FIXED BED COLUMN

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Abstract. The adsorption of Copper (II) and Chromium (III) from aqueous solution by natural zeolite was investigated in fixed bed column. The effects of selected operating parameters such as flow rate and bed depth were evaluated. The breakthrough data are fitted well to Bed Depth Service Time (BDST) and Thomas models with high correlation coefficient, R^2 = 0,91. The results showed that zeolite can be an effective adsorbent for Copper (II) and Chromium (III) removal.

Key words: copper, heavy metals, adsorption, wastewater

1. Introduction

The contamination of wastewater by toxic heavy metals is a worldwide environmental problem. Heavy metals are classified as toxic materials due to their non-biodegradability and bioaccumulation tendency in living organisms. Its excessive amount causes health problem in animals, plants and humans. These metals pollutants get to surface waters through different industrial enterprises activities. A number of techniques e.g. chemical precipitation, adsorption, ion exchange, and biological treatment have been applied. Although these techniques have been widely used, they possess limitations such as are high O&M cost and formation of by-products [1, 2]. Cu (II) and Cr (III) are essential for some biosynthesis in human body and are well-known as micronutrients for animals and plants, but they are toxic at high concentration. Recently, there is a growing interest in using zeolites as an adsorbent to remove heavy metals from wastewater. This method has been widely investigated as an alternative to current costly wastewater treatment methods [3, 4].

In previous publications the experimental studies of adsorption of heavy metal ions in static conditions were presented. The theoretical preconditions of the mechanism of sorption extract of cuprum and chromium from the investigated solution by clinoptilolite of Sokirnitsya deposit were defined. It has been established that the selectivity of metal extraction has an effect on the radius of the metal atom and the solubility of its compounds. The conditions of deposition of compounds of heavy metals have been established and a diagram of the composition of the investigated two-component system depending on the acidity of the medium was constructed [5, 6, 7].

2. Experimental studies

2.1. Characteristics of zeolite

The surface of zeolite after the adsorption of heavy metals was analyzed by X-ray fluorescence analyzer [8].

2.2. Adsorbent

For research the zeolite of Sokyrnytsya deposit (Ca–clinoptilolite) with the size ranging from 2–3 mm was used.

2.3. Adsorbate

Model solution of Cu (II) was prepared by dissolving of copper sulphate ($CuSO_4$ $5H_2O$) in distilled water. Model solution of Cr (III) was prepared by dissolving of chromium nitrate Cr(NO_3)$_3$ in distilled water. The initial concentration of the solution was 2.030 g/l. Concentrations of Cu (II) and Cr (III) in solutions were determined by atomic absorption spectroscopy.

2.4. Column Set-upa

A glass column with a diameter of 1 cm and a height of 50 cm was used. A known amount of adsorbent was placed into the column at the required adsorbent bed depth. Two cm thick fibreglass was placed at the bottom of the column to prevent the adsorbent media from leaching into and clogging the drainage area, as well as on the top of the adsorption column to increase the distribution of the solution onto the adsorbent surface and maintain a constant flow rate. The initial concentration of Cu (II) and Cr (III) solutions at 2,03 mg/l were pumped downward into the column. Lower concentration of metal ions solution was used to obtain a breakthrough curve as industrial effluents discharge are within this range [9, 10]. The column was operated until the concentration of metal ions in the effluents reached the value of about 2,03 mg/l . The column study was carried out at room temperature and all column experiments were performed in triplicates.

3. Results and Discussion

Analyzing the results of X-ray fluorescence analysis of the zeolite surface after adsorption of copper and chromium ions (Fig. 1), we see that copper ions are much better absorbed by the sorbent than chromium ions. Despite the uniform concentration of chromium and cuprum ions in the solution, selective extraction of Cu^{2+} occurs. As can be seen from the results of experimental studies. the concentration of copper ions on the surface of the sorbent increases from 0.682 % by weight at a concentration of 0.01 g/l to 47.380 % by weight at a concentration of 1 g/l. The concentration of chromium ions on the surface of the sorbent after adsorption was little dependent on the increase of Cr^{3+} concentration in the initial solution.

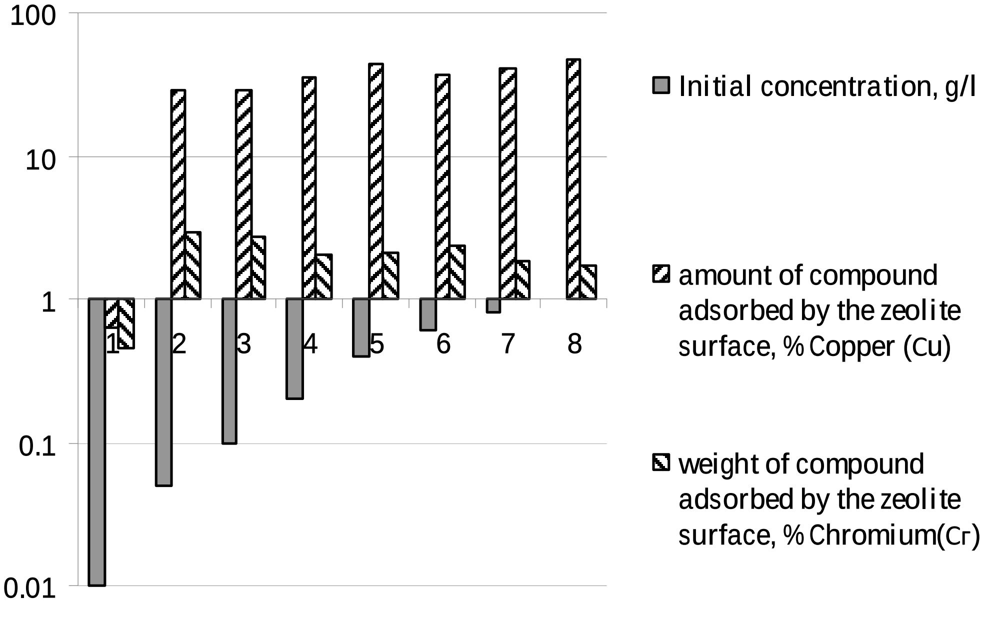
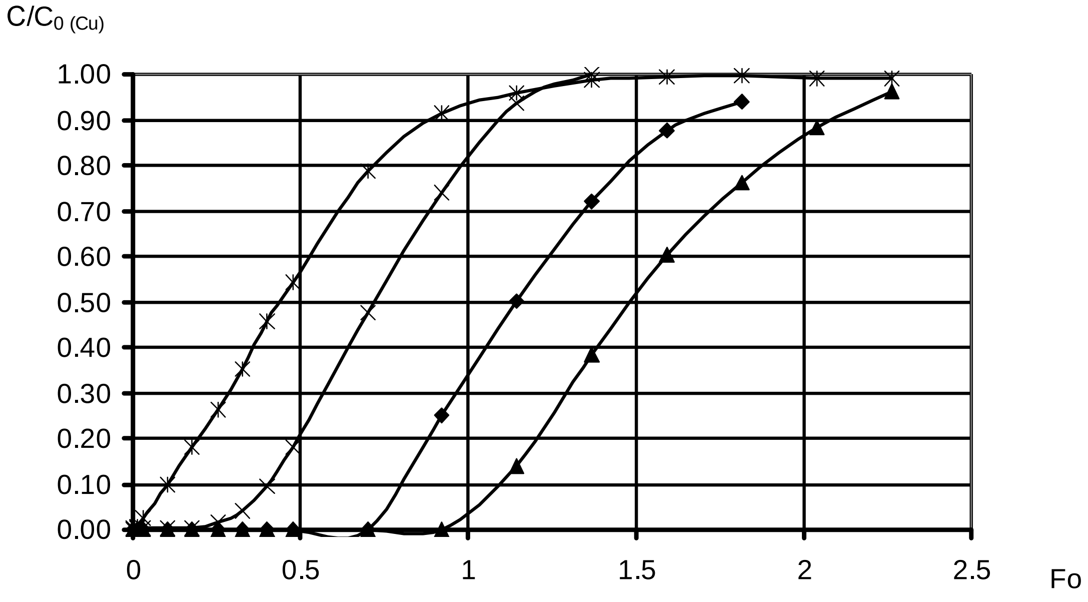


Fig. 1. The amount of copper and chromium ions on the surface of the sorbent after adsorption test solution

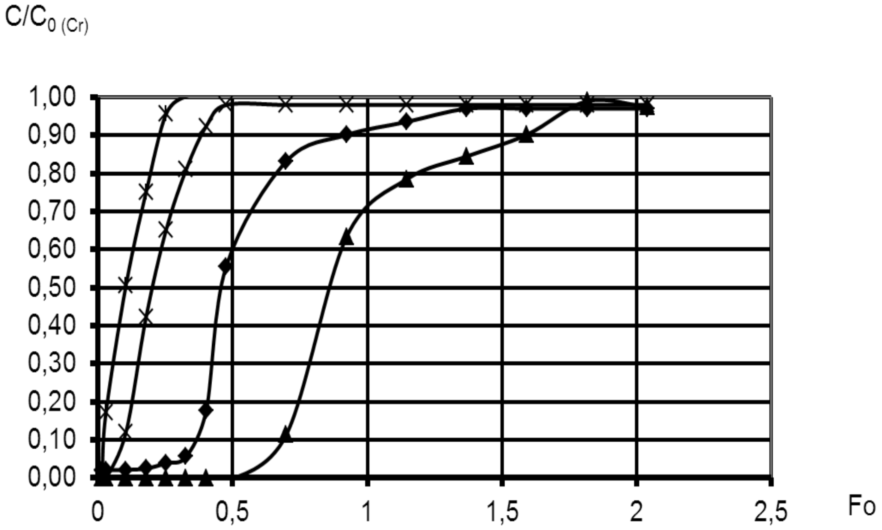
Effect of Bed Depth on Breakthrough Curve

Adsorption of heavy metals in the fixed bed column largely depends on the quantity of adsorbent in the column. As the bed depth increased, the volume of the treated solution and the amount of cuprum and chromium removal increased, respectively.

It can be seen that the breakthrough time (tb) and exhaustion time (te) increase with an increase in bed depth. Fig. 2 illustrates breakthrough curves obtained at different bed depth (2, 5 and 7 cm) with a constant concentration of 1 g/l and a flow rate of 4 ml/min. With the increase in the bed depth from 2 to 7 cm, the slope of the S-shaped curve decreased, since the height of the layer was increased, indicating that the initial curve becomes steeper when the bed depth decreases.



a



b

Fig. 2. Effects of different bed depth on the breakthrough curve of Cu (II) (a) and Cr (III) (b) adsorption onto zeolite at 4 ml/min flow rate:
*– 1 sm; x – 2 sm; ♦ – 5 sm; ▲ – 7 sm;

Table 1

Experiment constant of BDST model
for Cu (II) and Cr (III) adsorption onto zeolite
(C_0 = 2,030 g/l, flow rate = 4 ml /min)

Bed depth *(sm)*	a* Cu *(mg/g)*	*tb* Cu*(min)*	*te* Cu*(min)*	a* Cr *(mg/g)*	*tb* Cr*(min)*	*te* Cr*(min)*
2	8.93E+01	20	80	2.55E+01	2	30
5	9.91E+01	43	120	7.47E+01	15	55
7	9.49E+01	62	145	8.56E+01	30	80

The calculation of theoretical breakthrough curves was carried out on the following dependencies:

For the mathematical expression of the dependence between the concentration of copper and chromium ions and the time of sorption at a certain flow rate, we have used the Thomas (1) model, which is the simplest and most convenient. The equation of the output curve for a layer of low altitude was described by the following expression:

$$\frac{C}{C_0} = 1 - ae^{-lFo}, \qquad (1)$$

where λ is the model constant, 1 / s; a – coefficient of proportionality;

$Fo = \dfrac{D^{*}t}{R^{2}}$ – Fourier criterion;

D – coefficient of internal diffusion of heavy metals ions in the grain of adsorbent, m^2 / s; R – radius of the grain of adsorbent, m; t – time, s.

Values of $\dfrac{C}{C_0}$ for other bed depths Z was obtained on the basis of Laplace transformations, according to which a certain function N corresponding to the concentration varies according to the dependence [11]. Dependence (1) can describe the breakthrough curve for the bed depth Z-2cm.

$$N_n^{''} = \frac{1}{p}(pN^{1})^{n}, \qquad (2)$$

де

$$N^{'} = \frac{\lambda}{p(\lambda + p)}; \quad N^{''} = \frac{\lambda^{''}}{p(\lambda + p)^{n}};$$

p – Laplace parameter.

The transition to the original of the function was performed on the basis of transition tables from the image to the original. The original of the approximate solution has the form:

$$(\frac{C}{C_0})_n = 1 - \left[\lambda F_o + \frac{(\lambda F_0)^2}{2!} + \ldots + \frac{(\lambda F_0)^{n-1}}{(n-1)!}\right] e^{-\lambda F_0}, \qquad (3)$$

where n – layer targets lengths n = 2,3 ...

$Z_2 = nZ_{1.}$

After logarithm we get:

$$f(t) = 1 - e^{-aFo} \qquad (1)$$

$$\frac{x''}{x'} = 2; \quad f_2 = 1 - e^{-aFo}(1 + aFo)$$

$$\frac{x''}{x'} = n; \quad f_n = 1 - e^{-aFo}\left(1 + aFo + \ldots + \frac{aFo^{n-1}}{(n-1)!}\right) \qquad (2)$$

Analyzing experimental data, we see that in the initial moments of time, the experimental and theoretical curves coincide, but due to the large porosity of the granular layer (0.3), the solution is quickly filtered through the sorbent layer and the exhaustion time is almost equal to the breakthrough time. This process is described by the model of ideal displacement.

Conclusions

The elemental composition of the sorbent surface was investigated according to X-ray fluorescence method after absorption of heavy metals from a two-component system containing Cu^{2+} and Cr^{3+} ions. The mechanism of sorption of copper and chromium from a solution was theoretically grounded. It has been established that the selectivity of metal extraction has an effect on the radius of the element and the solubility of its hydroxides. The conditions of precipitation of the hydroxides of the corresponding metals were calculated and the logarithmic diagram of the composition of the two-component system was constructed, depending on the pH.

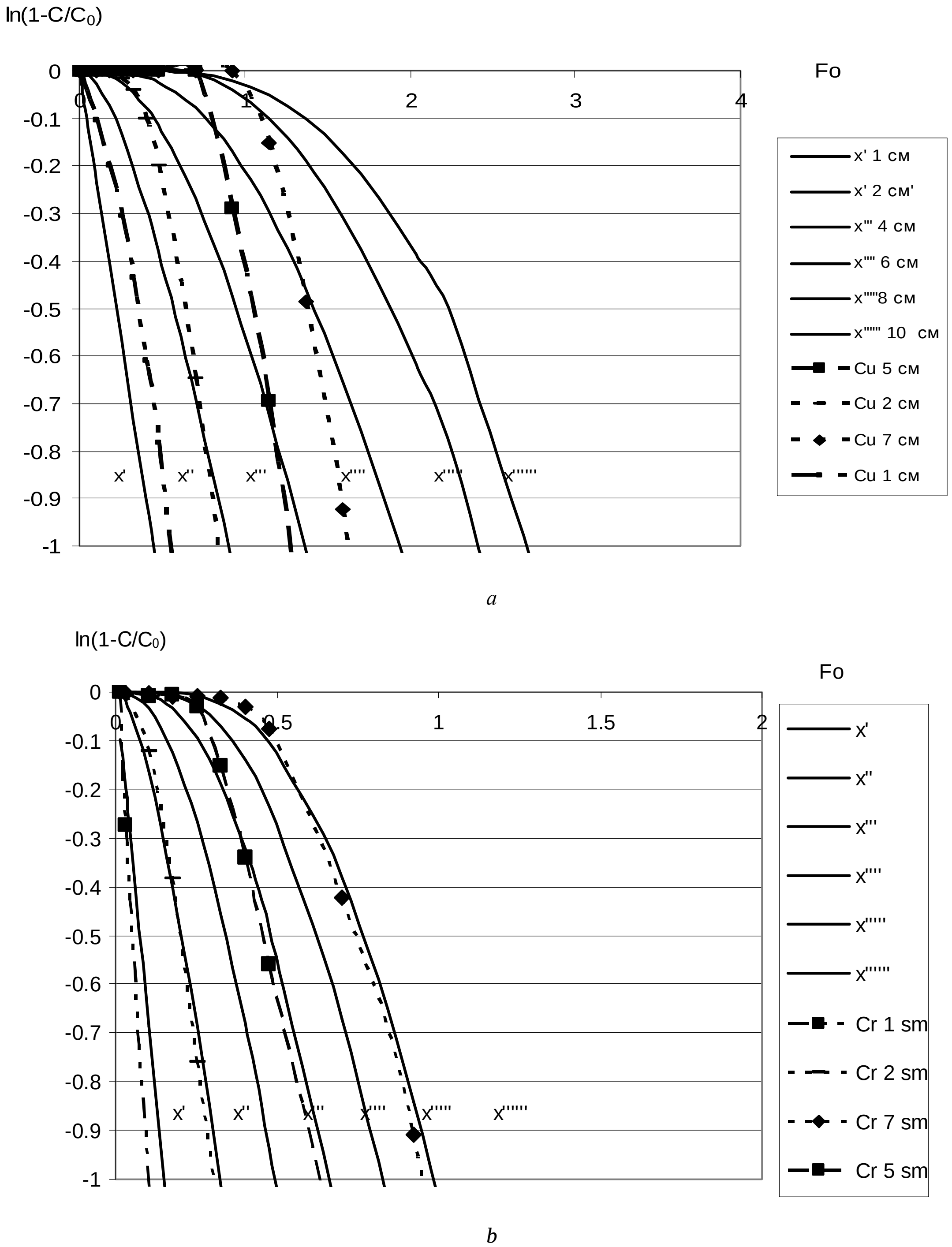


Fig. 1. Comparison of theoretical breakthrough curves of adsorption with experimental results in logarithmic coordinates
a – for Cu^{2+}; b – for Cr^{3+}, where * – 1 cm; x – 2 cm; ♦ – 5 cm; ▲ – 7 cm

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