

Sorption isotherms can be used to determine the nature of the distribution of metal ions between the adsorbent and the liquid phase in a state of equilibrium, depending on their concentration. In this study, in order to describe adsorption of heavy metal ions by chitosan-unithiol were applied the Langmuir and Freundlich isotherms.

The linearised form of Langmuir model is:

$$\frac{C_e}{A} = \frac{1}{A_{\infty}K_L} + \frac{1}{A_{\infty}}C_e \quad (1)$$

where K_L – equilibrium adsorption constant ($l \cdot mg^{-1}$), A_{∞} – limiting adsorption capacity ($mg \cdot g^{-1}$), A – adsorption ($mg \cdot g^{-1}$) and C_e – metal ion concentration in the solution at equilibrium ($mg \cdot l^{-1}$).

Freundlich's isotherm is an empirical equation that describes heterogeneous systems. The Freundlich model can be expressed by:

$$\ln A = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where K_F ($(mg \cdot g^{-1})(l \cdot g^{-1})^n$) is indicative of the relative sorption capacity and $1/n$ – is measure of the nature of the sorption, A – adsorption ($mg \cdot g^{-1}$) and C_e – metal ion concentration in the solution at equilibrium ($mg \cdot l^{-1}$).

On the Table 1 was illustrated the constant values for the corresponding sorption isotherms (Figure 2), calculated according to the Langmuir and Freundlich theories. According to the results, reported in Table 1, Langmuir equation best described the sorption of Cu (II) ions (correlation coefficients $R^2=0.934$). Therefore, according to the literature [19], all the sorbed particles interact only with the sorption centers and do not contact each other. For Pb (II) and Cr (VI) ions according to the regression coefficients proved that correlation of Freundlich model was strong with respect to the Langmuir model.

In the present work, pseudo-first-order and pseudo-second-order kinetic models were used to check the experimental data. The pseudo-first-order and pseudo-second-order models were described by the following equations:

$$\ln C_t = \ln C_0 - k_1 t \quad (3)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \quad (4)$$

where C_0 – initial concentration of metal ions, C_t – concentration of metal ions at time t . k_1 (min^{-1}) and k_2 ($ml \cdot mg^{-1} \cdot min^{-1}$) are rate constants.

Table 1 – Parameters of adsorption isotherms

Metal ions	pH	Langmuir isotherm			Freundlich isotherm		
		K_L ($l \cdot mg^{-1}$)	A_{∞} ($mg \cdot g^{-1}$)	R^2	K_F ($mg \cdot g^{-1})(l \cdot g^{-1})^n$	$1/n$	R^2
Cu (II)	4.5	53.94	1.03	0.934	1.74	0.31	0.765
Pb (II)	4.5	13.00	1.71	0.641	3.70	0.62	0.779
Cr (VI)	4.5	2.54	1.44	0.866	1.16	0.54	0.874

The constants were calculated from the slope and the intercept of the plots are given in Table 2 and Figure 3. The results are given in Table 2 illustrate that for both Cu (II) and Cr (VI) ions, the R^2 values ($R^2 = 0.999$ and 0.983) for pseudo-first-order model higher than results obtained using pseudo-second-order model ($R^2=0.950$ and 0.892). Thus, the pseudo-first-order model explains the kinetics better. But kinetics of sorption Pb (II) ions is better described by pseudo-second-order model ($R^2 = 0.941$). Heavy metals such as lead, copper, chromium are poisons for the body.

They enter the human body not only in an individual form, but also in the joint presence of metals. Getting into the human body, they cause symptoms of poisoning: headache, vomiting, convulsions. Therefore, in this paper, the sorption process was studied in the joint presence of the Cu (II), Pb (II) and Cr (VI) ions, the result of which is given below.

Thus, the results of sorption show that the degree of chromium removal was reached 90%. Hence, this composite proved to be effective in the removal of chromium ions.