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[1*] A. N. Imangaliyeva, [1] G. A. Seilkhanova, [1] A. Zh. Ondasheva, [1] M. S. Telkhozhayeva

[1]Al-Farabi Kazakh National University, Faculty of Chemistry and Chemical Technology,
Al-Farabi av. 71, 050040, Kazakhstan, Almaty,
e-mail: imangaly.ainur@gmail.com

Adsorption studies of Cu (II), Pb (II) and Cr (VI) by chitosan/unitiol composite

Abstract: Chitosan-unithiol composite for the first time was synthesized by simple and short period procedure. The sorption process was carried out under static conditions at temperature 298 K and at pH=4.5. The concentration of ions of toxic metals before and after sorption was determined by the atomic absorption method. The removal characteristics such as the removal degree and equilibrium time of Cu^{2+}, Pb^{2+} and Cr^{6+} were illustrated. The adsorption equilibrium for Cu^{2+} ions was best described by Langmuir model and for Pb^{2+} and Cr^{6+} ions by Freundlich model. It was found that adsorption of Cu^{2+} and Cr^{6+} by chitosan-unithiol followed first-order kinetics. Adsorption of Pb^{2+} was followed second-order kinetics. The sorption process was also investigated under co-presence of heavy metal ions. The obtained results indicate that the synthesized chitosan-unithiol composite is the effective sorbent for removing toxic metal ions.

Key words: sorption, composite, chitosan, unithiol, degree of removal.

Introduction

One is the main purpose of the adsorption of heavy metals is to find an effective modification method of material. The synthesized material has to be approach to several requirements such as low toxicity, high biocompatibility, adsorption capacity, selective sorption and the absence of side effects during the sorption [1]. In recent years the application of biomaterials such as algae, bacteria, fungi, high plants, and products derived from these organisms have represented big interest [2].

Chitosan is a natural polysaccharide widely used in fundamental studies as well as practical applications, including in treatment of wastewater, heterogeneous catalysts, delivery vaccines materials, agricultural stimulators, antibacterial agent and medical entersorbents [3], [4]. It consists of β-(1→4)-linked D-glucosamine and *N*-acetyl-D-glucosamine units. Chitosan is a well-known adsorbent for toxic and heavy metal ions. Due to the lone pair of electrons on nitrogen in acetoamido group and hydroxyl group can posse high chelating ability. Furthermore, the ability of chitosan depending on the acidity of the medium to form flaky precipitation can be used in sorption. For instant, in the recent years biosorbents based on chitosan has been synthesized and their sorption characteristics were studied for use in separation of heavy metal ions. Intoxication by heavy metal ions can lead to serious diseases of organism. These metal ions non-degradable and are persistent in the medium. Therefore chitosan has been applied in the synthesis various functional composites, by using clays, inorganic substances, natural and synthetic polymers [5].

In this way, a system which consists of chitosan and polyvinyl alcohol was studied. It was found that the adsorption efficiency of this sorbent has the maximum recovery of cadmium ions at pH = 6 and t = 40 C [6].

Also, in the work [7] the adsorption of composite material composed from chitosan and polyvinyl chloride was demonstrated. One of the advantages of this polymer is physical and chemical stability in organic solutions as well as in concentrated acidic and alkaline media. The study showed that the adsorption capacity of the chitosan and polyvinyl chloride system were 90% for Cu (II) and Ni (II) [7]. In the study [8] effect of modification by different compounds were illustrated. For instant, sorption activities of chitosan compounds were increased according to the following sequence: chitosan-cotton [9], [10], chitosan-magnetite [11], chitosan-cellulose [12], chitosan-perlite [13], chitosan-alginate [14], [15] and chitosan- clinoptilolite [16].

It is known that unithiol (2,3-Dimercapto-1-propanesulfonic acid) is widely used in medicine as an antidote drug against heavy metal and radionuclide ions. Unithiol was found to have good solubility in water and strong chelation by virtue of sulfhydryl group [17]. Despite these additional features, unithiol has a disadvantage due to its high price.

Thus, using the positive features of both chitosan and unithiol materials, the novel chitosan-unithiol composite was synthesized. The sorption of heavy metal ions by chitosan-unithiol composite was investigated. This work was done with the purpose to establish the effect of concentration of metal ions and kinetics of sorption process. In our work was also shown the capability of chitosan-unithiol to sorb copper, lead and chromium ions during their simultaneous presence.

Materials and methods

Chitosan flakes with the deacetylation degree of about 85% and molecular weight of 3,00,000 produced from crab shells (Tokyo Chemical Industry UK Ltd) were used for experiments. Uniothiol in ampoules with a concentration of 50 mg/ml ("Belmed drugs", Belarus) were used as a modifier.

Preparation of chitosan-unithiol composite was carried out as follows:

An aqueous solution of chitosan was prepared by dissolving chitosan (0.25 g) in 5 ml of acetic acid (75 wt. %) for 30 min. And then 5 ml of H_20 and 5 ml of acetic acid (75 wt. %) were added in course of stirring. Chirosan after keeping 1 day at room temperature was put on 100 cm^3 solution of unithiol with concentration of 1 mg/ml.

All the experiments were carried out under bath conditions with solutions containing $CuCl_2$, $Pb(NO_3)_2$, $K_2Cr_2O_7$. Sorption was performed in 100 ml vessels by pouring metal ions containing solutions onto 1 g of chitosan-unithiol composite and occasional stirring.

The concentration of Cu (II) and Pb (II) before and after sorption was determined by the AAS method using an atomic absorption spectrophotometer «Shimadzu 6200». Cr (VI) concentrations were determined photometrically on the Specord 200 (Analytic Jena) at λ=530 nm using 1,5 -diphenylcarbazide as an indicator.

Results and discussion

The removal degree is an important characteristic because it shows efficiency of the sorbent. Sorption of Cu2+, Pb2+ and Cr 6+ ions by initial chitosan and unithiol-chitosan was investigated at 25 °C in the time interval from 0 to 180 min and results are provided in Figure 1. The addition of a modifier to the sorbent composition significantly increased the recovery of metal ions, practically reaching 100 %, while the initial chitosan recovered only about 80 % of the ions. On the course the time the initial concentration of metals was reduced. After 3 hours removal degree of ions were achieved the maximum extent. Hence 3 hours was found to be equilibrium sorption time.

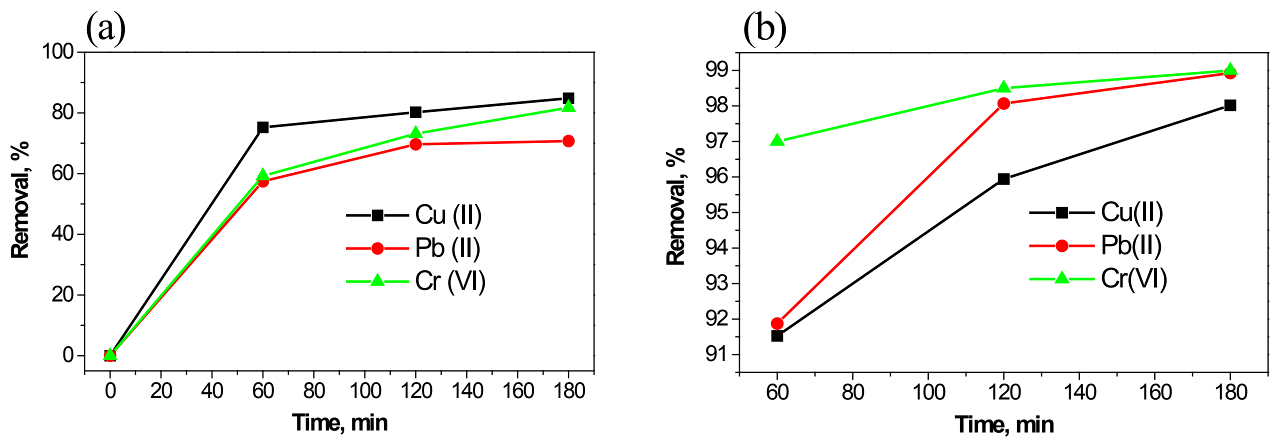

Figure 1 – Adsorption characteristics of (a) chitosan and (b) chitosan-unithiol composite for Cu (II), Pb (II) and Cr (VI) ions

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·mg^{-1}), A_∞ – limiting adsorption capacity (mg·g^{-1}), A – adsorption (mg·g^{-1}) and C_e – metal ion concentration in the solution at equilibrium (mg·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·g^{-1})(l·g^{-1})^n) is indicative of the relative sorption capacity and 1/*n* – is measure of the nature of the sorption, A- adsorption (mg g^{-1}) and C_e – metal ion concentration in the solution at equilibrium (mg·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:

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

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

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 mg^{-1} min^{-1}) are rate constants.

Table 1 – Parameters of adsorption isotherms

Metal ions	pH	Langmuir isotherm			Freundlich isotherm		
		K_L (l mg^{-1})	A∞ (mg g^{-1})	R^2	K_F (mg g^{-1})(l 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.

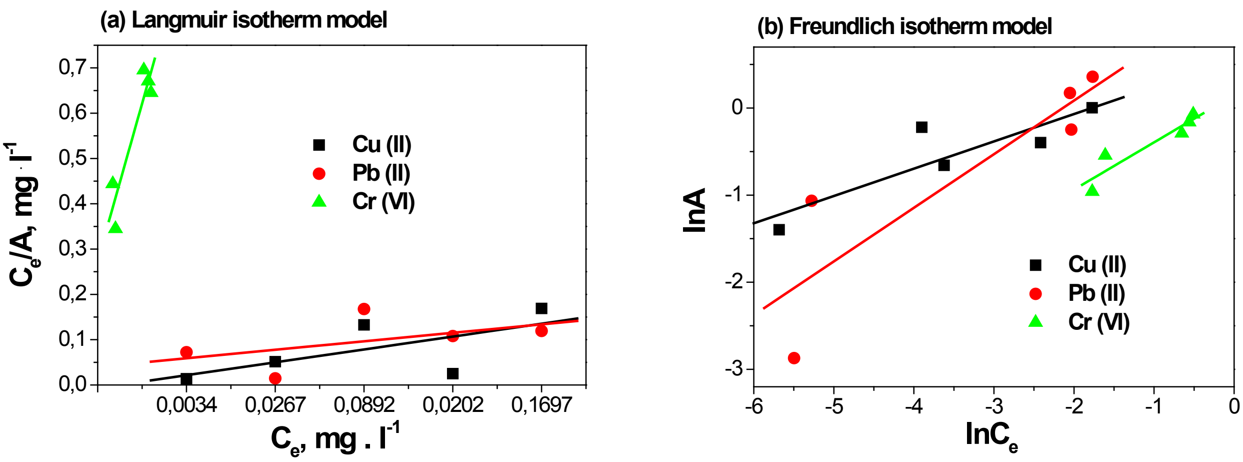

Figure 2 – (a) Langmuir and (b) Freundlich isotherm adsorption model of the Cu (II), Pb (II) and Cr (VI)

Table 2 – Kinetic characteristics of adsorption of metal ions

Metal ion	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
	C_0 (mg/l)	k_1 (min^{-1})	R^2	C_0 (mg/l)	C_0 (mg/l)	k_2 (l mg^{-1} min^{-1})	R^2
Cu (II)	6.13	0.014	0.999	5.21	0.04	0.618	0.950
Pb (II)	4.44	0.003	0.918	7.94	0.25	0.025	0.941
Cr (VI)	6.24	0.015	0.983	2.00	0.03	0.694	0.892

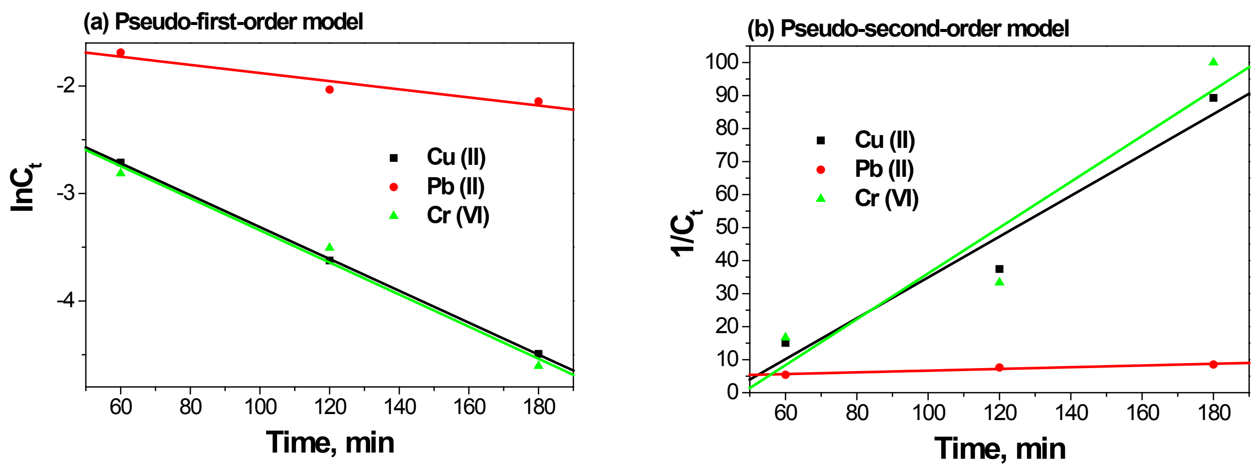

Figure 3 – Plots of (a) pseudo-first-order and (b) pseudo-second-order kinetics of sorption by chitosan-unithiol composite

Table 3 – The results of sorption at a joint presence of metal ions

Metal ions	Removal, %	Adsorption capacity, mg/g
Cu (II)	25	$2.5\ 10^{-4}$
Pb (II)	30	$11.4\ 10^{-4}$
Cr (VI)	90	$40.5\ 10^{-4}$

Conclusion

In the present work, synthesis of a sorbent based on chitosan and unithiol for the first time was reported. Analysis of the sorption characteristics of the obtained composite showed a significant increasing of adsorption. The removal degrees of Cu (II), Pb (II), and Cr (VI) ions were equal to 98%, 99% and 99%, respectively. It was found that the Langmuir isotherm better describes the sorption of Cu (II) ions than the Freundlich isotherm, which indicates the formation of a monomolecular sorption layer. Freundlich isotherm displayed a better fitting model than Langmuir isotherm for adsorption of Pb (II) and Cr (VI). The kinetic process can be predicted by pseudo-first-order model and rate constants for Cu^{2+} and Cr^{6+} sorption were found to be 0.014 and 0.015 min^{-1}, respectively at 25°C. Adsorption of Pb^{2+} was followed second-order kinetics and rate constant were equal to 0.025 l mg^{-1} min^{-1}. The effect of sorbent on the joint presence of heavy metal ions showed high sorption properties respect to Cr (VI) ions. The removal degrees are Cr^{6+} – 90%, Pb^{2+}-30%, Cu^{2+}-25%. The obtained results show that this material is a highly effective composite for the removal of toxic metal ions.

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