BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Tomul LVI (LX), Fasc. 4, 2010
Secţia
CHIMIE şi INGINERIE CHIMICĂ

KINETICS STUDY OF LEAD(II) ADSORPTION ON CHITOSAN

BY

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Abstract. In this study the adsorption of lead(II) from aqueous solutions on chitosan was investigated, from kinetic point of view. The influence of contact time, in optimum experimental conditions was studied in batch experiments. The obtained results have shown that the chemical interactions between metal ions and functional groups from chitosan surface might be the rate-limiting elementary process. The experimental data were analyzed using three kinetics models: pseudo-first order Lagregen model, pseudo-second order Ho model and intra-particle diffusion model. On the basis of these models, the kinetics parameters (rate constant and equilibrium adsorption capacity) for lead(II) ions adsorption on chitosan were calculated.

Key words: lead(II), adsorption, chitosan, kinetics.

1. Introduction

Chemical precipitation, coagulation, ion exchange, membrane filtration, flocculation are the main methods used for the removal of metal ions from aqueous effluents. But, many of these methods are relatively expensive and non-environmental friendly, because require additional reagents, or generate important quantities of secondary wastes [1], [2].

In regards of its simplicity and high-efficiency characteristics, the adsorption is looked upon as a better technology [3]. The potential of some low-cost materials, including agricultural or industrial wastes, for the removal of toxic metal ions from aqueous solutions, makes this method economically feasible and in some cases very useful [4], [5].

The chitosan is one example of such adsorbent, which is very efficient in removing various toxic and strategic metal ions, such as cadmium, mercury, molybdenum, uranium, vanadium, platinum, palladium, etc. [6],…,[8]. Chitosan is a hydrophilic natural polymer produced by alkaline deacetilation of chitin, obtained mainly by extraction from shrimp and crab shells, and is considered the most abundant bio-polymer occurring in nature, after cellulose [9]. The utilization of such environmental-friendly material for the removing of extremely toxic metal ions (as lead(II)) is one of the areas of growing interest, especially in the environment and industrial field.

In this study, the kinetics of lead(II) adsorption from aqueous solutions on chitosan, was investigated. The influence of contact time, in optimum experimental conditions, was studied in batch experiments. The experimental data were analyzed using three kinetics models: pseudo-first order Lagregen model, pseudo-second order Ho model and intra-diffusion particle model. On the basis of these models, the kinetics parameters (rate constant and equilibrium adsorption capacity) were calculated.

2. Experimental

2.1. Materials

All chemical reagents were of analytical degree and were used without further purifications. The stock solution of lead(II) containing 2000 mg Pb(II)· L^{-1} was prepared by lead nitrate (Reactivul Bucharest) dissolving in twice distilled water. The working solutions were obtained by diluting the stock solution with distilled water. The initial pH value of work solutions was obtained using acetate buffer (CH_3COOH/CH_3COONa) with pH = 6.0.

The chitosan used as adsorbent in this study was purchased from Vanson (M_w = 755.900, polydispersity index = 1.82, acetylation degree = 20.8%) and was dried in air (6 h, at 70 ± 3°C), and then stored in a desiccators.

2.2. Methods

The adsorption experiments were performed by batch technique, at room temperature (20 ± 2°C), mixing samples of cca. 0.125 g of chitosan with volumes of 25 mL solution of 169.07 mg Pb(II)·L^{-1}. The initial pH of working solutions was obtained by adding 5.0 mL of acetate buffer (pH = 6.0). After a determined period of time with intermittent stirring, the phases were separated by filtration, and the lead(II) concentration in filtrate was determined spectrophotometrically with 4-(2-pyridylazo)-resorcinol (Digital Spectrophotometer S 104 D, λ = 530 nm, 1 cm glass cell, against blank solution) [10], using a prepared calibration graph. The lead(II) adsorption efficiency was evaluated using amount of lead(II) adsorbed on weight unit of adsorbent (q, mg·g^{-1}) and adsorption yield (R, %), calculated according with their definition [11].

2.3. Kinetics Models

The experimental results were analyzed using the following kinetics models: pseudo-first order Lagregen model [12], pseudo-second order Ho model [13], [14] and intra-particle diffusion model [15].

The kinetics equation of pseudo-first order Lagregen model is:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

and its linear form can be written as:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303}t \tag{2}$$

where: k_1 is the rate constant for the pseudo-first order kinetics model; q_e, q_t – the amounts of lead(II) retained on weight unit of chitosan at equilibrium and at time t, respectively.

In case of pseudo-second order kinetics model, the rate equation may be formulated as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

and the linear form of this is:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{4}$$

where: k_2 is the rate constant for the pseudo-first order kinetics model; q_e, q_t – the amounts of lead(II) retained on weight unit of chitosan at equilibrium and at time t, respectively.

The kinetics equation of intra-particle diffusion model is:

$$q_t = k_{dif} \cdot t^{1/2} + c \tag{5}$$

where: k_{dif} is the intra-particle diffusion rate constant, c is the concentration of lead(II) from solution at equilibrium, q_t – the amount of lead(II) retained on weight unit of chitosan, at time t. The values of k_{dif} and c can be calculated from the slope and intercept of q_t *versus* $t^{1/2}$ dependence.

3. Results and Discussions

In a previous study [16] it has show that the chitosan can be successfully used for lead(II) removal from aqueous solutions, and the efficiency of adsorption process depends by the initial solution pH and adsorbent dose. On the basis of these experimental results we have considered that the optimum conditions for lead(II) adsorption on chitosan are an initial solution pH = 6.0 (acetate buffer) and an adsorbent dose of 5 g chitosan $\cdot L^{-1}$. Under these conditions, the value of removal yield varied between 98.57% (for an initial lead(II) concentration of 42.26 $mg \cdot L^{-1}$) and 63.47% (when initial lead(II) concentration is 676.28 $mg \cdot L^{-1}$).

Another important parameter, is special for kinetics point of view, is the contact time of the two phases. The influence of the contact time between adsorbent (chitosan) and aqueous solution which contains 169.07 mg $Pb(II) \cdot L^{-1}$, on the removal efficiency is presented in Fig. 1.

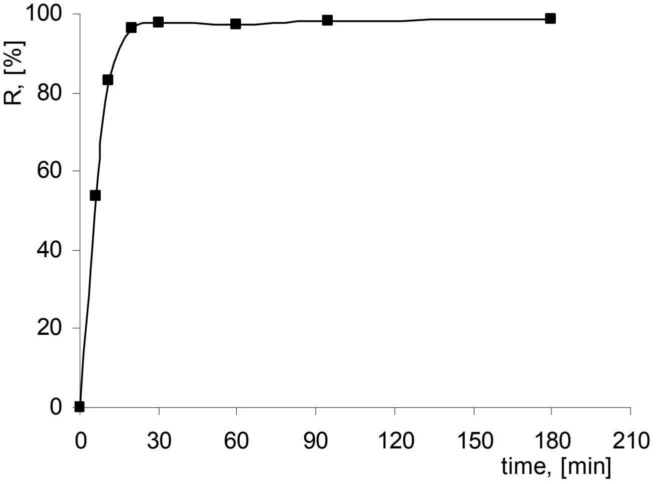

Fig. 1 – Removal yield of lead(II) onto chitosan as a function of contact time.

The experimental results indicate that in mentioned experimental conditions, the adsorptive removal of lead(II) on chitosan increase with the increasing of contact time. The adsorption rate is faster during of initial stages, in the first 20 min being retained around 96.55% from initial lead(II) concentration. After this initial stage, the adsorption process becomes slower near to equilibrium, which is practically obtained after 80 min.

These observations suggest that the adsorption process of lead(II) is controlled by chemical interactions between metal ion (Pb^{2+}) and functional groups from chitosan surface.

In order to analyzed the kinetics of adsorption process of lead(II) on chitosan, the pseudo-first order Lagregen model, pseudo-second order Ho model and intra-particle diffusion model, were applied to the experimental data.

The graphical representation of the linear forms for the pseudo-first order and the pseudo-second order kinetics models are presented in Figs. 2 and 3, and the values of kinetics parameters, calculated from the slope and intercept of these dependences, together with the values of correlation coefficients (R^2) foe each case, are summarized in Table 1.

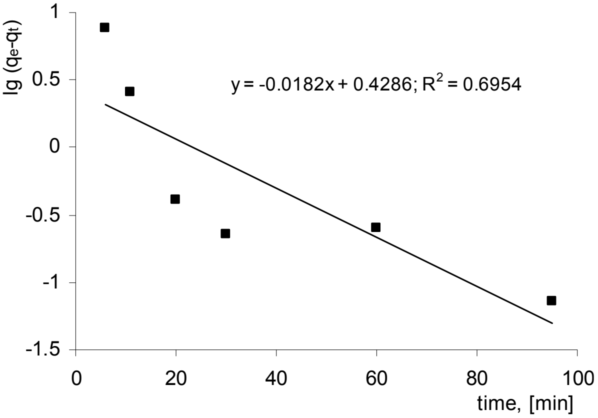

Fig. 2 – Pseudo-first order Lagregen model representation for lead(II) adsorption on chitosan.

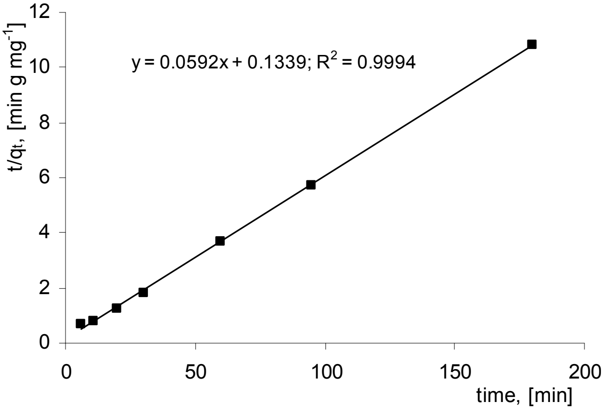

Fig. 3 – Pseudo-second order Ho model representation for lead(II) adsorption on chitosan.

It can be observed from Fig. 2 and Table 1, that in case of pseudo-first order kinetics model utilization, the values of correlation coefficient is lower

(0.6954) and the value of equilibrium adsorption capacity (q_e, [mg·g^{-1}]) calculated from this equation is much lower that the experimental value (q_e^{exp}, [mg·g^{-1}]). Under these conditions, the pseudo-first order Lagregen model is not suitable for to describe the kinetics of lead(II) adsorption from aqueous solutions on chitosan.

Table 1

The Values of Kinetics Parameters Obtained from Linear Dependences Presented in Figs. 2 and 3

q_e^{exp} [mg·g^{-1}]	Lagregen model			Ho model		
	R^2	q_e [mg·g^{-1}]	k_1 [min^{-1}]	R^2	q_e [mg·g^{-1}]	k_2 [g·mg^{-1}·min^{-1}]
16.6272	0.6954	2.6828	7.903 10^{-3}	0.9994	16.8918	2.617 10^{-2}

The experimental data were further fitted by the pseudo-second order Ho model (Fig. 3), and better fitting was obtained. By using this model, the value of correlation coefficient (R^2) is higher, and the calculated equilibrium adsorption capacity (q_e, [mg·g^{-1}]) is similar with the experimental value (q_e^{exp}, [mg·g^{-1}]).

All these observations and the experimental results presented above indicate that the lead(II) adsorption on chitosan occurs according with the pseudo-second order kinetics, where the rate-limiting elementary process is the chemical interactions between metal ion and functional superficial groups of adsorbent.

If the intra-particle diffusion is the rate-limiting elementary process, the amount of metal ion retained on weight unit of adsorbent varies with the square root of time. The graphical representation of dependence q_t *versus* $t^{1/2}$, obtained in case of lead(II) adsorption on chitosan (Fig. 4) does not go through the origin, and two separated regions were obtained.

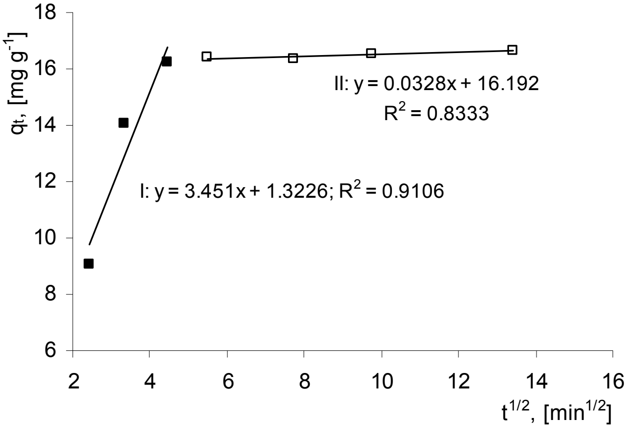

Fig. 4 – The representation of intra-particle diffusion kinetics model for lead(II) adsorption on chitosan.

Both separately regions were separately evaluated using eq. (5), and the values of k_{dif} and c, calculated from the slopes and intercepts are summarized in Table 2.

Table 2

The Values of Kinetics Parameters Obtained from Intra-Particle Diffusion Model for Lead(II) Adsorption on Chitosan

Region I			Region II		
R^2	c, [mg·L^{-1}]	k_{dif}, [min^{-1}]	R^2	c, [mg·L^{-1}]	k_{dif}, [min^{-1}]
0.9106	1.3226	3.4510	0.8333	16.1920	$3.280\ 10^{-2}$

The deviation of the straight lines from origin indicates that the intra-particle diffusion process is not the rate-controlling step, but the boundary layer diffusion controls the adsorption in some degree. In addition, the higher values of rate constants obtained from this model (in comparison with the pseudo-second order model) is another argument which sustain that the intra-particle diffusion process not limited the rate of lead(II) adsorption on chitosan.

The multi-linearity obtained in this case indicated that two or more elementary steps occur in the adsorption process. The first region is attributed to the fast transfer of lead(II) ions from bulk solution to the adsorbent surface, and the second region to the intra-particle diffusion on adsorbent.

4. Conclusions

In this study, the adsorption of lead(II) from aqueous solutions on chitosan was investigated from kinetics point of view. The experimental results have shown that the efficiency of lead(II) adsorption on chitosan depends by initial solution pH, chitosan dose and initial lead(II) concentration. The best values of removal yield were obtained at pH = 6.0 (acetate buffer) and a chitosan dose of 5 g·L^{-1}.

The contact time required for the maximum adsorption is near to 80 min. This indicates that the adsorption process of lead(II) ions is controlled by the chemical interactions between metal ions (Pb^{2+}) and superficial functional groups of chitosan.

From kinetics point of view, the experimental data obtained in case of lead(II) adsorption on chitosan are very well fitted by pseudo-second order Ho model, which confirm the chemical nature of the rate-limiting elementary process. The high value of rate constant indicates that the lead(II) adsorption on chitosan is a relative fast process.

Received: October 10, 2010

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REFERENCES

1. Patterson J.W., *Industrial Wastewater Treatment Technology*. Butterworth Publishers, Stoneham, MA, 321, 1985.
2. Mendoza C.A., Cortes G., Munoz D., *Heavy Metal Pollution in Soils and Sediments of Rural Developing District 063, Mexico.* Environ. Toxicol. Wat. Qual., **11**, *4*, 327−333 (1998).
3. Gogate P.R., Pandit A.B., *A Review of Imperative Technologies for Wastewater Treatment II: Hybrid Methods.* Advanced Environ. Res., **8**, 553–597, 2004.
4. Babel S., Krniavan T.A., *Low Cost Adsorbents for the Heavy Metals Uptake from Contaminated Water: a Review*, J. Hazard. Mater., **B 97**, 219–243 (2003).
5. Igwe J.C., Abia A.A., *A Bioseparation Process for Removing Heavy Metals from Waste Water Using Biosorbents.* Afr. J. Biotechnol., **5**, *12*, 1167−1179 (2006).
6. Varma A.J., Deshpandea S.V., Kennedy J.F., *Metal Complexation by Chitosan and its Derivatives: a Review, Carbohydrate Polym.*, **55**, 77–93 (2004).
7. Wan Ngah W.S., Endud C.S., Mayanar R., *Removal of Copper(II) Ions from Aqueous Solution onto Chitosan and Cross-Linked Chitosan Beads.* Reactive and Functional Polymers, **50**, 181–190 (2002).
8. Justia K.C., Fávere V.T., Laranjeira C.M.M., Nevesa A., Peralta R.A., *Kinetics and Equilibrium Adsorption of Cu(II), Cd(II), and Ni(II) Ions by Chitosan Functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formyl-phenol.* J. Coll. Interf. Sci., **291**, 369–374 (2005).
9. Guibal E., *Interactions of Metal Ions with Chitosan-Based Sorbents: a Review*, Sep. Purif. Technol., **38**, 43–74 (2004).
10. Flaska A.H., Barnard A.J., *Chelates in Analytical Chemistry.* Marcel Dekker Inc. New York, 231, 1976.
11. Dean J.A, *Analytical Chemistry Handbook.* McGraw-Hil, Inc., New York. 3. 52, 1995.
12. Febrianto J., Kosasih A.N., Sunarso J., Ju Y.H., Indrawati N., Ismadji S., *Equilibrium and Kinetic Studies in Adsorption of Heavy Metals Using Biosorbent: A Summary of Recent Studies.* J. Hazard Mat., **162,** 616–645 (2009).
13. Ho Y.S., Porter J.F., McKay G., *Equilibrium Isotherm Studies for the Sorption of Divalent Metal Ions onto Peat: Copper, Nickel and Lead Single Component Systems.* Water, Air and Soil Pollution, **141**, 1−33 (2002).

14. Ho Y.S., McKay G., *The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat.* Water Res., **34**, 735–742 (2000).
15. Cheung W.H., Szeto Y.S., MgKay G., *Intraparticle Diffusion Processes During Acid Dye Adsorption onto Chitosan.* Bioresour. Technol., **98**, 2897–2904 (2007).
16. Asandei D., Bulgariu L., Bobu E., *Lead(II) Removal from Aqueous Solutions by Adsorption on Chitosan.* Cell. Chem. Technol., **43**, 211–216 (2009).

STUDIUL CINETIC AL ADSORPŢIEI PLUMBULUI(II) PE CHITOSAN

(Rezumat)

În acest studiu a fost investigată adsorbția plumb(II) din soluții apoase pe chitosan, din punctul de vedere cinetic. Influența timpului de contact, în condiții experimentale optime a fost studiat prin tehnica discontinuă. Rezultatele obținute au arătat că interacțiunile chimice între ionii metalici şi grupe funcționale de pe suprafata chitosanului ar putea fi procesul determinat de viteză. Datele experimentale au fost analizate cu ajutorul a trei modele cinetice: modelul de ordin pseudo-unu Lagregen, modelul de ordin pseudo-doi Ho şi modeulul difuziei intra-particulă. Pe baza acestor modele, parametri cinetici (constanta de viteză şi capacitatea de adsorbție la echilibru) au fost calculate pentru adsorbția plumb(II) pe chitosan.