Chitosan and Chitosan Modified with Glutaraldehyde Microparticles for Pb(II) Biosorption

II. Equilibrium and kinetic studies

CLAUDIA MARIA SIMONESCU[1]*, IRINA MARIN[1], CHRISTU TARDEI[2], MIOARA DRAGNE[3], CAMELIA CAPATINA[4]

[1]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Analytical Chemistry and Environmental Engineering, 1 – 7 Polizu Str., 011061, Bucharest, Romania

[2]National Institute for R&D in Electrical Engineering ICPE-CA, 313 Splaiul Unirii, 031066, Bucharest, Romania

[3] SC KEMWATER CRISTAL SRL, 51 Muncii Str., 915200, Fundulea, Călăraşi, Romania

[4]University „Constantin Brâncuşi" of Târgu-Jiu, Engineering Faculty, 3 Geneva Str., 210152, Târgu-Jiu, Gorj, Romania

This paper presents a comparative study regarding the use of chitosan and cross-linked with glutaraldehyde (GLA) chitosan microparticles in the retention of Pb(II) ions from aqueous solutions with low Pb(II) levels. Initial Pb(II) ion concentration, contact time, and pH are parameters considered. Sorption capacity value reaches 43.78 mg Pb(II)·g^{-1} for chitosan particles, and 41.68 mg Pb(II)·g^{-1} for chitosan-GLA particles, respectively. Equilibrium sorption data for Pb(II) removal onto chitosan, and chitosan-GLA were consistent with the Langmuir isotherm. Kinetic parameters for the pseudo-first and pseudo-second orders and intraparticle diffusion equations were determined. Pb(II) sorption on chitosan microparticles can be expressed as a pseudo-second order kinetic which characterizes a chemical process. A different kinetic behaviour function of Pb(II) concentration was observed for chitosan-GLA microparticles. Results show that microparticles obtained can be successfully used for remediation of wastewater with low lead content.

Keywords: chitosan microparticles, chitosan-GLA microparticles, lead removal from wastewater, equilibrium and kinetic studies

Water quality represents a major concern worldwide. Water effluents contaminated with heavy metals have been extensively studied due to their negative effects on natural ecosystems equilibrium and living organisms.

The main sources of heavy metals pollution are: metal cleaning and plating facilities, mining, corrosion and electronic device manufacture, paints, battery manufactures, petroleum refining, fertilisers, leather industry [1, 2]. Among all heavy metals, special attention has given to lead due to its negative effects on humans such as mental retardation, kidney diseases, semi-permanent brain damage and many other symptoms [3-5]. As a result, lead has to be removed from wastewater in order to prevent natural waters pollution.

Many conventional treatment methods such as chemical precipitation, ion exchange, sorption, electrochemical technologies, and membrane separation were applied to remove lead from wastewaters [6-21]. All these methods show several disadvantages such as high operating costs, incomplete lead removal, low selectivity, inadequate for lead removal from wastewater with low lead level, and production of large quantities of wastes [22-25]. The most popular method for the removal of heavy metal from aqueous solutions is sorption using biomaterials. Several biomaterials like grape stalk waste [26], three wastes [27], the aquatic plant, *Lemna perpusilla* Torr. [28], ethylene-diamine-modified yeast biomass coated with magnetic chitosan microparticles (EYMC) [29], native and chemically treated olive stone [30] were used for lead removal from aqueous solutions.

The use of natural biomaterials is a promising alternative due to their low cost and their relative abundance. The adsorption capacities of these adsorbents are dependent on the porosity, surface area-to-volume ratio, and number of active binding sites [31].

Polysaccharide biopolymers are mainly used as adsorbents of heavy metals from aqueous solutions. They are generally derived from agricultural or shell waste from crustaceans. Chitin is a biopolymer found in crustaceans, fungi, insects, annelids, molluscs and coelenterata [31]. Chitin abundance is second to cellulose and it is used to obtain chitosan by deacetylation. Metal ions chelating capacity of chitosan depends on chitin deacetylation degree. Increasing the deacetylation degree of chitin leads to the increasing of chitosan metal chelating capacity [32]. This property is related to the content of the amino groups in the polymer chain, and the degree of polymerisation of oligochitosan. The main disadvantages of use of chitosan for heavy metals removal from wastewaters are low porosity and its low stability in acidic media (pH<2) that determines inconveniencies in adsorbent removal from treated effluents.

Physical and chemical modifications of chitosan are used to overcome this disadvantage. For this purpose, chitosan microparticles were previously obtained by physical modification of chitosan flakes. Chemically modified chitosan microparticles were obtained by cross-linking with GLA to improve its solubility in acidic media (pH<2) [33]. These microparticles previously obtained were characterized and tested for resistance against acid, alkali and other chemicals [33].

Results obtained showed that physical modification of chitosan flakes has as results improving the mechanical strength, and chemical modification enhances its resistance against acid solutions.

* *email: claudiamaria_simonescu@yahoo.com*

The specific relationship between methods used in preparation of chitosan and chitosan based materials for wastewater treatment needs further examination.

In this study we employed chitosan and chitosan-GLA microparticles for Pb(II) removal from aqueous solutions with low Pb(II) concentrations. The influence of initial *p*H of Pb(II) ions solution, contact time, and initial concentrations on the Pb(II) ions uptake were approached. The linear Langmuir and Freundlich isotherms were used to fit the equilibrium sorption data. The sorption rates were determined quantitatively and compared by the pseudo-first order, pseudo-second order and intraparticle diffusion models. Results can be useful for further applications in the treatment of industrial wastewater.

Experimental part

Samples of chitosan and chitosan-GLA microparticles were used for lead removal from aqueous solutions. Chitosan and chitosan-GLA particles were previously obtained by chemical precipitation and analyzed by FT-IR spectroscopy, SEM and TG/DSC before the use of Pb(II) ions removal [33].

Dissolving the corresponding salt ($Pb(NO_3)_2$) (Merck a.r. grade) in distilled water stock solutions of 1000 mg·L^{-1} of Pb(II) were prepared. Aqueous working solutions of Pb(II) were prepared by diluting the stock solutions with distilled water to get the desired lead concentrations.

Biosorption experiments were made by means of a batch method using a GFL 3019 stirrer at 150 rpm (rotation per min) speed rotation. The following parameters: 0.01 g chitosan samples, the 10 mL Pb(II) solutions at 5–100 mg·L^{-1} Pb(II) concentration at time varied from 5 to min 180 min were used.

Metallic ion concentration in initial solutions, and in solution after the biosorption on chitosan were determined by atomic absorption spectrometry using a type AAS 1N Carl Zeiss Jena Atomic Adsorption Spectrophotometer.

The effect of contact time at room temperature was also studied. The effect of *p*H on the uptake of Pb(II) ions from aqueous solution was studied, too. Different values of *p*H from 2.5 up to 7 were applied into the aqueous solution for the optimum contact time that was determined from the previous step. The *p*H of the initial 10 mL solution of Pb(II) was adjusted to the required *p*H value using appropriate concentrations of HNO_3 0.1N or NaOH 0.1N solutions.

The experimental values obtained were fitted using the Langmuir and Freundlich equilibrium equations.

Results and discussions

Experiments in batch mode were carried out to determine the influence of process parameters on the biosorption of chitosan and chemical modified chitosan. The following parameters: the contact time, the concentration of Pb(II) ions in the initial solution, and the *p*H of the solution were examined.

The contact time effect

It is well known that the contact between the pollutants and absorbent is of significance importance in wastewater treatment processes using sorption technology. Sorbent efficiency is given by adsorption speed, and by the time needed to reach the equilibrium. Consequently, it is important to establish the optimum contact time between two phases (pollutants and adsorbent) for future design of wastewater treatment system.

The effect of contact time on the amount of biosorption was investigated over the range from 5 to 180 min with five initial Pb(II) concentrations of 5, 10, 25, 50 and 100 mg·L^{-1}. The experiments were performed for chitosan and chitosan-GLA microparticles (chitosan:GLA = 1:2 molar ratio).

The sorption capacity of a sorbent, Q, was determined from equilibrium studies and using the mass balance (equation 1):

$$Q=\frac{(C_i-C_f)V}{m} \quad (1)$$

where

Q is the sorption capacity, mg·g^{-1};

C_i - initial metal ion concentration, mg·L^{-1};

C_f - metal ion concentration in solution at different times, mg·L^{-1};

V - solution volume, L;

m - sorbent mass, g.

The adsorption data for lead uptake by chitosan and chitosan-GLA microparticles versus contact time is shown in figure 1a and b.

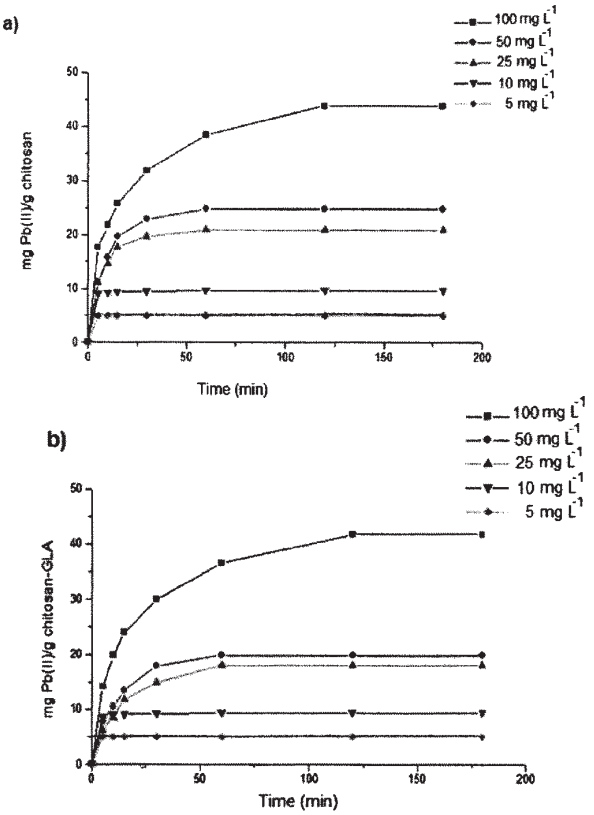

Fig. 1. The effect of contact time on the biosorption of Pb(II) ions onto chitosan microparticles (a), and chitosan-GLA microparticles (b)

The uptake amount of Pb(II) increases with contact time but after 60 min of contact time the increase is slow, indicating that the equilibrium is almost reached after 60 min. Therefore, the optimum contact time for adsorption of Pb(II) can be considered 60 min. The reason is that, after 60 min, free binding centers of chitosan and chitosan-GLA started to be saturated with lead ions. For the same adsorbent, but different lead concentration can be observed that the biosorptions, in terms of mg·g^{-1} were increased by increasing the initial lead concentration. This is due to the fact that the initial concentration of lead ions provides an important driving force to overcome all mass transfer resistance of lead between the aqueous and solid phases [34].

Comparing figure 1a with 1b it can be observed that cross-linking of chitosan with GLA determines decreasing of chitosan biosorption capacity. The maximum amount of Pb(II) ions retained by chitosan is 43.78 mg·g^{-1} for

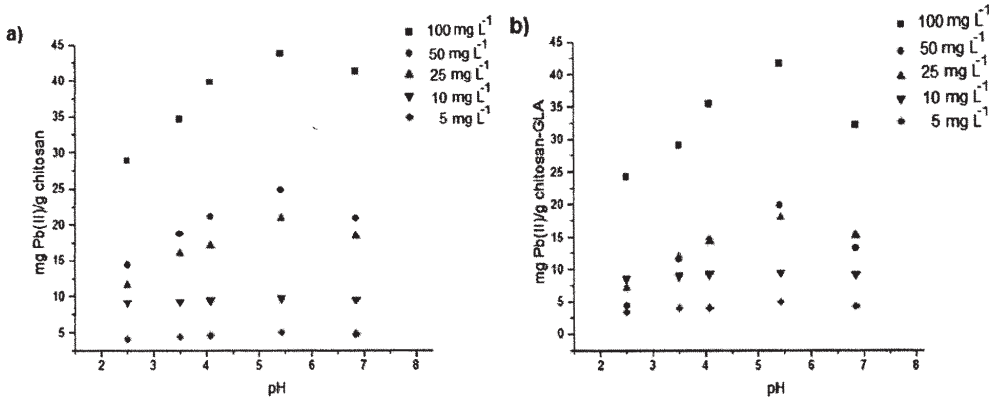

Fig. 2. The effect of *p*H on the biosorption of Pb(II) ions onto chitosan microparticles (a), and chitosan-GLA microparticles (b)

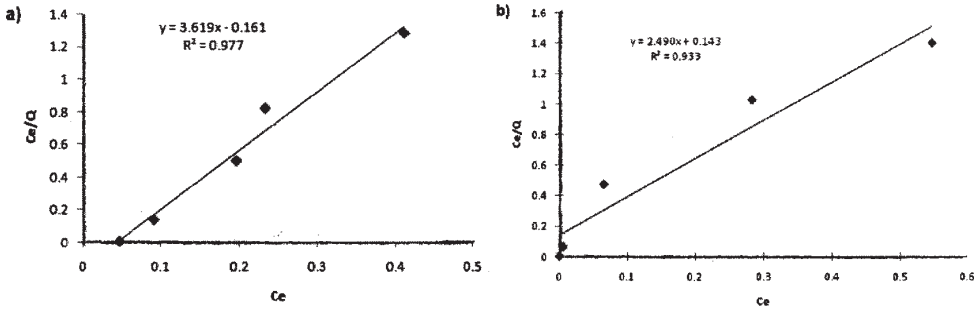

Fig. 3. Langmuir linearized isotherm for Pb(II) sorption on chitosan microparticles (a) and on chitosan-GLA microparticles (b)

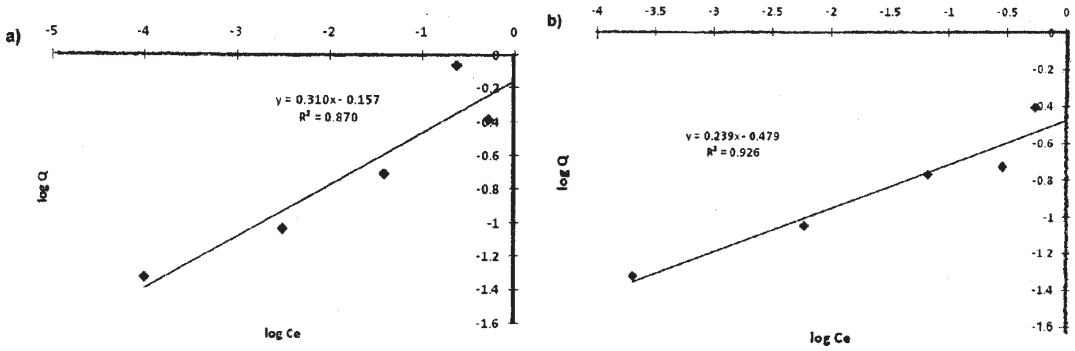

Fig. 4. Freundlich linearized isotherm for Pb(II) sorption on chitosan microparticles (a) and on chitosan-GLA microparticles (b)

chitosan microparticles, and 41.68 mg·g^{-1} for chitosan-GLA microparticles. These values are close to those mentioned in literature data [35].

Effect of pH

The initial *p*H range was set between 2.5-7 due to the formation of insoluble hydroxide $Pb(OH)_2$ at *p*H values higher than 7. The results are presented in figure 2.

As it is shown in figure 2a and b, the biosorption of Pb(II) ions is highly dependent on the *p*H of the metal solution. This is due to the fact that *p*H can affect the solubility of the metal ions and influences the ionization state of the functional groups existing on the biosorbent [35]. It is well known that solutions with low *p*H values contain more protons available to protonate amine groups from chitosan to form groups $-NH_3^+$. Thus, the number of binding sites for the biosorption of Pb(II) ions will decrease. Moreover, the protonation of amino groups induced, and electrostatic repulsion of Pb(II) ions [36]. There is a competition between Pb(II) ions and protons from the acidic solution. This trend was also observed in case of chitosan-GLA microparticles (fig. 2b). The low biosorption capacity of chitosan-GLA microparticles is due to cross-linking of amine sites with aldehyde groups that will not be available for further biosorption of Pb(II) ions.

At higher *p*H, biosorption of Pb(II) increases due to the decreased inhibitory effect of H^+, which decreases with the increase in *p*H. The maximum biosorption of Pb(II) on chitosan and chitosan-GLA were found at 5.4. At *p*H values higher than 7, Pb(II) precipitation occurred.

Equilibrium sorption isotherm

Equilibrium isotherm has an important role in describing the interactive behaviour between the solutes and sorbent, but also is fundamental in the design of the adsorption system [37]. Adsorption isotherms give the relationship between the amount of a substance adsorbed at constant temperature.

Equilibrium sorption isotherms are usually described by the Langmuir and Freundlich models. The most widely used Langmuir equation characterizes monolayer sorption onto a surface with a finite number of identical sites. Moreover, Langmuir model is based on the assumption that there is no interaction between the adsorbate molecules. Langmuir model is represented by the following equation:

$$Q = \frac{K_L \cdot C_e}{1 + a \cdot C_e} \quad (2)$$

where:

Q - the maximum adsorption at monolayer (mg·g^{-1});

C_e - the equilibrium concentration of Pb(II) (mg·L^{-1});

K_L and *a* are the Langmuir model parameters.

The following equation was obtained by linerization of equation (2):

$$\frac{C_e}{Q} = \frac{1}{K_L} + \left(\frac{a}{K_L}\right) \cdot C_e \quad (3)$$

Values of Langmuir parameters (K_L and a) were determined from graphic Ce/Q= f(Ce) (fig. 3). Freundlich equation based on sorption on a heterogeneous surface is

Sorbent	Langmuir parameters			Freundlich parameters		
	Q (mg·g^{-1})	a (mL·mg^{-1})	R^2	K_F (mg·g^{-1})	n	R^2
Chitosan microparticles	43.78	574	0.977	14.35	3.1	0.870
Chitosan-GLA microparticles	41.68	403	0.933	10.16	4.18	0.926

Table 1
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS AND CORRELATION COEFFICIENTS

represented by:

$$Q = K_F \cdot C_e^{1/n} \quad (4)$$

where:

K_F and n are Freundlich constants that show sorption capacity and intensity, respectively.

The following equation was obtained by logarithmation of Freundlich equation:

$$\log Q = \log K_F + n \log C_e \quad (5)$$

A linear plot of logQ against log Ce (fig. 4) was used to obtain K_F and n values.

In table 1 are shown the values calculated of the Langmuir and Freundlich isotherm constants.

The correlation coefficients obtained from Langmuir and Freundlich models suggest that the biosorption of Pb(II) on the chitosan and cross-linked chitosan microparticles correlated well (R>0.977; R > 0.933) with the Langmuir equation under the concentration range studied. The higher agreement with Langmuir isotherm indicates that Pb(II) biosorption on chitosan and cross-linked chitosan microparticles can be described as a monolayer adsorption.

Kinetics of biosorption

For the kinetic studies, samples containing chitosan/ chitosan-GLA microparticles and Pb(II) solutions were removed from the shaker between 5 min and 180 min. These tests were performed in order to verify sorption kinetic models and to establish the mechanism of sorption and potential rate controlling steps. These are useful for selecting optimum operating conditions for the full-scale batch process. Three models, such as the pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion model were used to fit the kinetic data.

The pseudo-first-order model assumes that the rate of adsorption on sorbent is proportional to the number of active sites available on to adsorbent media.

The pseudo-first-order model [38] is given by Lagergren equation:

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \quad (6)$$

where:

Q_e, Q_t are the sorption capacities at equilibrium and at time t (mg·g^{-1}), and k_1 is the rate constant of pseudo-first order sorption (min^{-1}).

The pseudo first-order model was made in linear form by logarithmation (equation 7):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} \cdot t \quad (7)$$

where:

Q_e and Q_t represent the amounts of Pb(II) sorbed on sorbent (mg·g^{-1}) at equilibrium and at time t, respectively and k_1 is the rate constant of first-order sorption (min^{-1}). Data obtained were used to draw the graphic $\log(q_e - q_t) = f(t)$. Rate constant, k_1 and correlation coefficient, R, values for Pb(II) biosorption were determined from it (figs. 5 and 6).

The values obtained for k_1, and R for the pseudo-first-order Lagergren model are presented in table 2.

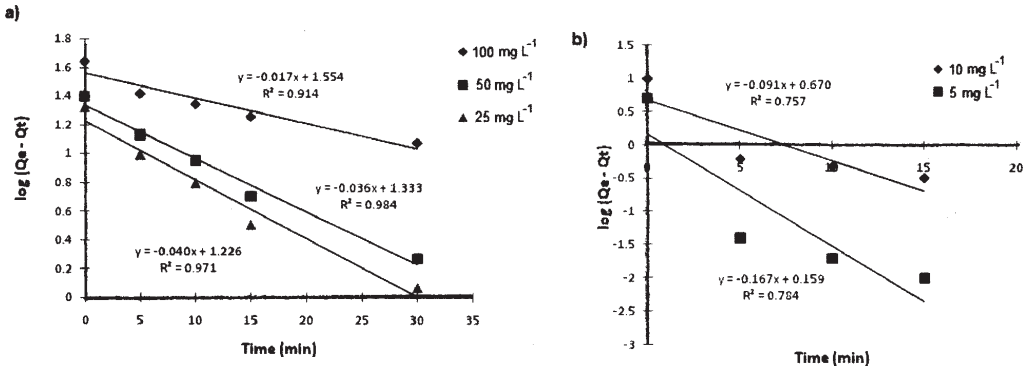

Fig. 5. Pseudo-first order sorption kinetics Pb(II) onto chitosan at 100 mg·L^{-1} initial concentration, 50 mg·L^{-1} initial concentration, 25 mg·L^{-1} initial concentration (a) 10 mg·L^{-1} initial concentration , and 5 mg·L^{-1} initial concentration (b)

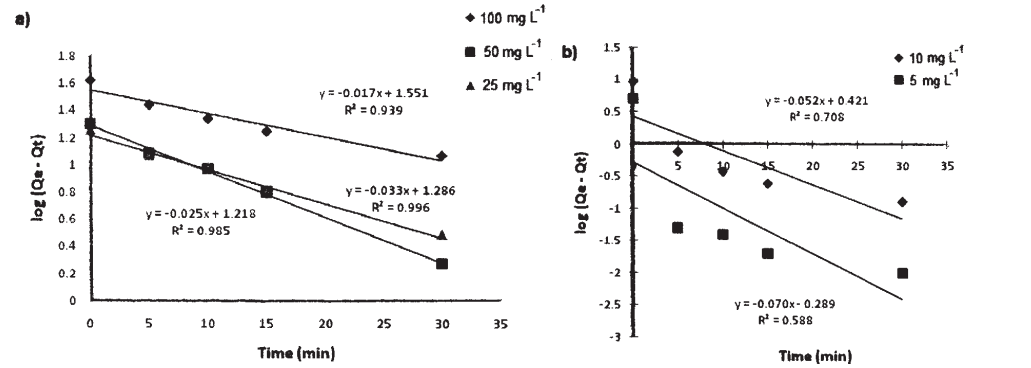

Fig. 6. Pseudo-first order sorption kinetics Pb(II) onto chitosan-GLA at 100 mg·L^{-1} initial concentration, 50 mg·L^{-1} initial concentration, 25 mg·L^{-1} initial concentration (a) 10 mg·L^{-1} initial concentration , and 5 mg·L^{-1} initial concentration (b)

Table 2

THE RATE CONSTANT K_1 AND R CORRELATION COEFFICIENT VALUES FOR PSEUDO-FIRST-ORDER EQUATION

Sorbent	100 mg Pb(II) L^{-1}		50 mg Pb(II) L^{-1}		25 mg Pb(II) L^{-1}		10 mg Pb(II) L^{-1}		5 mg Pb(II) L^{-1}	
	k_1 (min^{-1})	R^2	k_1 (min^{-1})	R^2	k_1 (min^{-1})	R^2	k_1 (min^{-1})	R^2	k_1 (min^{-1})	R^2
chitosan	$3.9151 \cdot 10^{-2}$	0.914	$8.2908 \cdot 10^{-2}$	0.984	$9.212 \cdot 10^{-2}$	0.971	$2.0957 \cdot 10^{-1}$	0.757	$3.846 \cdot 10^{-1}$	0.784
Chitosan-GLA	$3.9151 \cdot 10^{-2}$	0.939	$5.7575 \cdot 10^{-2}$	0.985	$7.5999 \cdot 10^{-2}$	0.996	$1.1976 \cdot 10^{-1}$	0.708	$1.6121 \cdot 10^{-1}$	0.588

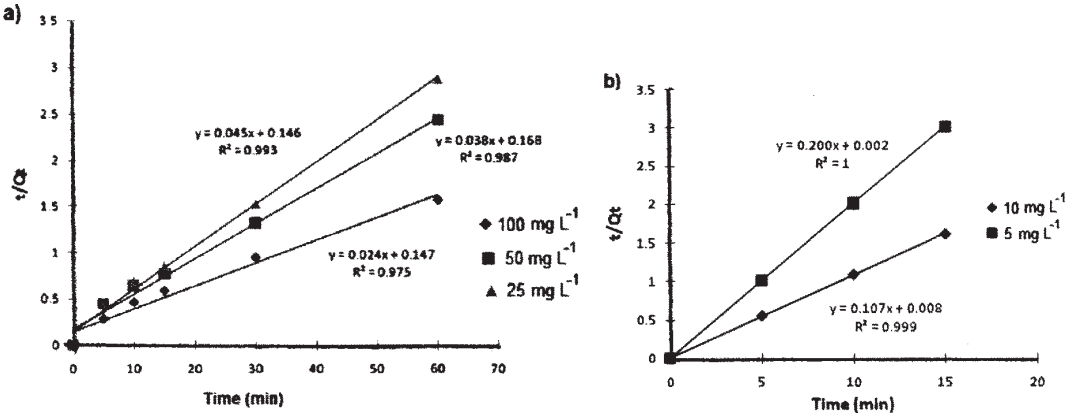

Fig. 7. Pseudo-second order sorption kinetics Pb(II) onto chitosan at 100 $mg \cdot L^{-1}$ initial concentration, 50 $mg \cdot L^{-1}$ initial concentration, 25 $mg \cdot L^{-1}$ initial concentration (a) 10 $mg \cdot L^{-1}$ initial concentration, and 5 $mg \cdot L^{-1}$ initial concentration (b)

The second-order equation [39] is given in the following equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (8)$$

k_2 being the rate constant of second-order adsorption ($g \cdot mg^{-1} \cdot min^{-1}$). Straight-line plots t/Q_t against t (figs. 7 and 8) were used to obtain rate parameters. The results can be used to show the applicability of this kinetic model to fit the experimental data.

The second-order sorption rate constant (k_2) and the correlation coefficient (R) values obtained from the experimental data are shown in table 3.

The intraparticle diffusion rate [40] is given by:

$$Q_t = k_i t^{0.5} \quad (9)$$

where k_i is intraparticle diffusion rate ($mg \cdot g^{-1} \cdot min^{-0.5}$).

The k_i is the slope of straight-line portions of the plot of Q_t against $t^{0.5}$. Intraparticle diffusion kinetic for Pb(II) biosorption on chitosan and chitosan-GLA is presented in figures 9 and 10.

Table 4 presents the value of k_i determined from experimental data.

The pseudo-second-order model was found to be in better agreement with experimental data regarding the kinetics of Pb(II) ions biosorption by chitosan compared to pseudo-first-order and intraparticle diffusion.

This kinetic considered that the rate determining step is chemical adsorption and not the mass transfer because the correlation coefficient (R^2) varies from 0.975 to 1.

Pb(II) biosorption by chitosan-GLA can be described in terms of intraparticle diffusion for 100 mg Pb(II)·L^{-1} solution (R^2 = 0.965), and in terms of the equation of pseudo-order I for 50 and 25 mg Pb(II)·L^{-1} (R^2 = 0.985, and R^2 = 0.996). Equation of pseudo-order II describes kinetic for 10 mg Pb(II)·L^{-1} and 5 mg Pb(II)·L^{-1} (R^2 = 1, and 0.999). Thus, if, for chitosan microparticles sorption kinetic does not

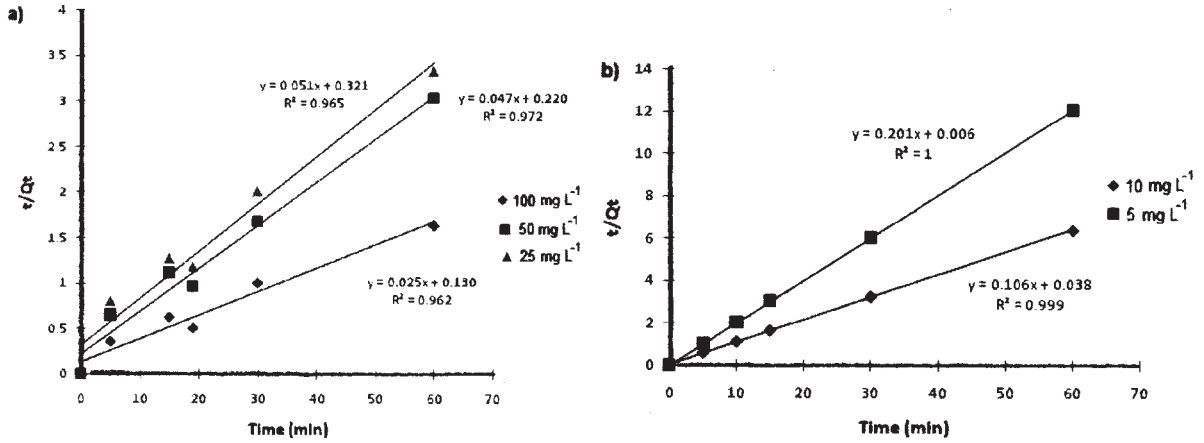

Fig. 8. Pseudo-second order sorption kinetics Pb(II) onto chitosan-GLA at 100 $mg \cdot L^{-1}$ initial concentration, 50 $mg \cdot L^{-1}$ initial concentration, 25 $mg \cdot L^{-1}$ initial concentration (a) 10 $mg \cdot L^{-1}$ initial concentration , and 5 $mg \cdot L^{-1}$ initial concentration (b)

Table 3

THE RATE CONSTANT K_2 AND R CORRELATION COEFFICIENT VALUES FOR PSEUDO-SECOND-ORDER EQUATION

Sorbent	100 mg Pb(II) L^{-1}		50 mg Pb(II) L^{-1}		25 mg Pb(II) L^{-1}		10 mg Pb(II) L^{-1}		5 mg Pb(II) L^{-1}	
	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2
chitosan	$3.918 \cdot 10^{-3}$	0.975	$8.5952 \cdot 10^{-3}$	0.987	$1.3869 \cdot 10^{-2}$	0.993	1.4311	1	2	0.999
Chitosan-GLA	$4.808 \cdot 10^{-3}$	0.962	$1.0041 \cdot 10^{-2}$	0.972	$8.1028 \cdot 10^{-3}$	0.965	$4.8077 \cdot 10^{-3}$	1	2	0.999

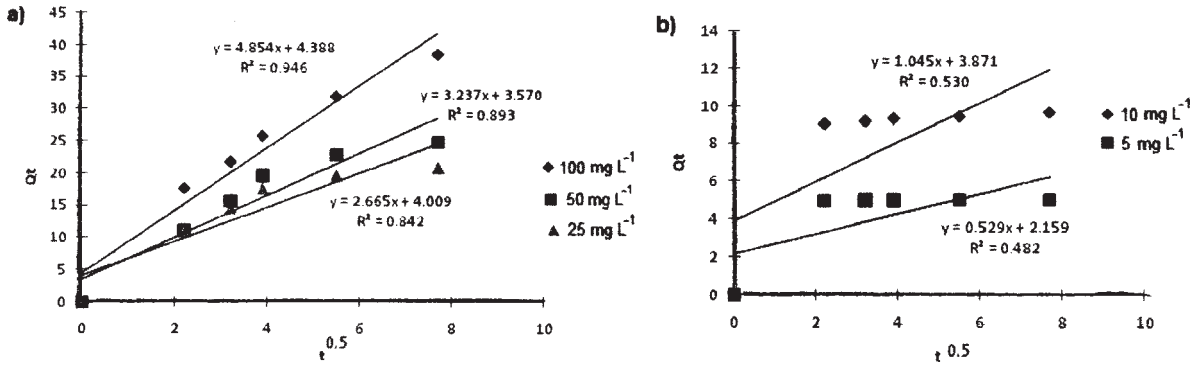

Fig. 9. Intraparticle diffusion sorption kinetics of Pb(II) onto chitosan at 100 mg·L^{-1} initial concentration, 50 mg·L^{-1} initial concentration, 25 mg·L^{-1} initial concentration (a) 10 mg·L^{-1} initial concentration , and 5 mg·L^{-1} initial concentration (b)

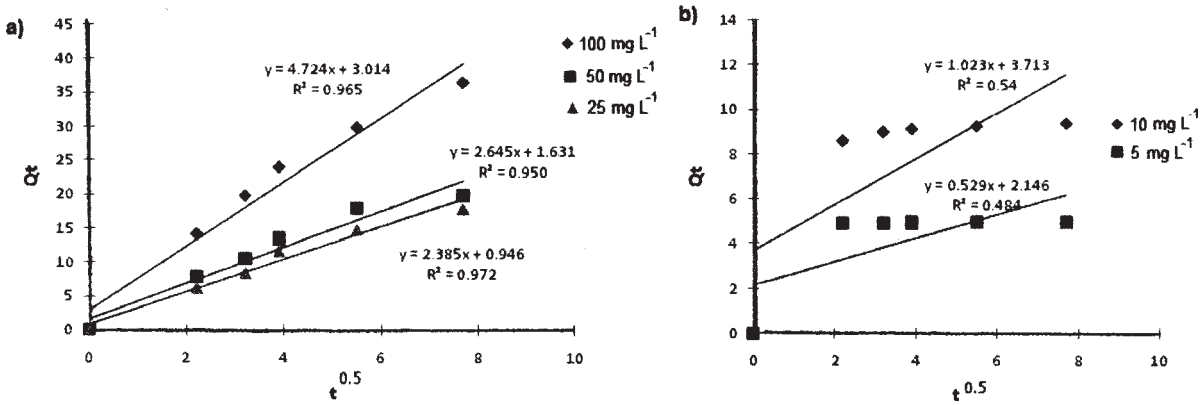

Fig. 10. Intraparticle diffusion sorption kinetics of Pb(II) onto chitosan-GLA at 100 mg·L^{-1} initial concentration, 50 mg·L^{-1} initial concentration, 25 mg·L^{-1} initial concentration (a) 10 mg·L^{-1} initial concentration, and 5 mg·L^{-1} initial concentration (b)

Table 4

THE RATE CONSTANT K_i AND R CORRELATION COEFFICIENT VALUES FOR INTRAPARTICLE DIFFUSION EQUATION

Sorbent	100 mg Pb(II) L^{-1}		50 mg Pb(II) L^{-1}		25 mg Pb(II) L^{-1}		10 mg Pb(II) L^{-1}		5 mg Pb(II) L^{-1}	
	k_i (mg·mg^{-1}·min$^{-0.5}$)	R^2	k_i (mg·mg^{-1}·min$^{-0.5}$)	R^2	k_i (mg·mg^{-1}·min$^{-0.5}$)	R^2	k_i (mg·mg^{-1}·min$^{-0.5}$)	R^2	k_i (mg·mg^{-1}·min$^{-0.5}$)	R^2
chitosan	4.854	0.946	3.237	0.893	2.665	0.842	1.045	0.530	0.529	0.482
Chitosan-GLA	4.724	0.965	2.645	0.950	2.385	0.972	1.023	0.54	0.529	0.484

depend on Pb(II) concentration in aqueous solution, for chitosan-GLA microparticles Pb(II) biosorption kinetic depends on Pb(II) level.

Conclusions

A comparative experimental study has been performed to evaluate sorption capacities of physically and chemically modified chitosan. Equilibrium sorption properties were investigated for both sorbents. The sorption process achieved equilibrium after 60 min.

The values obtained for the maximum amount of Pb(II) retained·g^{-1} of sorbent are close to those present in the literature data. The amino groups of chitosan are protonated at low *p*H values, and are not available for Pb (II) binding. Pb(II) ions sorption equilibrium can be described in terms of Langmuir model.

Sorption process of Pb(II) ions by chitosan microparticles can be described in terms of second order kinetics. This kinetic considered that the rate determining step is chemical sorption. A different behaviour in terms of sorption kinetics has been found for chitosan-GLA microparticles. Sorption of Pb(II) by chitosan-GLA is a chemical sorption for low Pb(II) ions concentration, a physical sorption for medium concentrations, and an intraparticle diffusion for high Pb(II) ions level.

From this comparative study, it can be concluded that cross-linking of chitosan with GLA has as results decreasing of chitosan biosorption capacity, but increase of stability in acidic solution and therefore a more easy separation by simple filtration from treated waters. This decrease of biosorption capacity is not significant.

The research findings in this study suggest the suitability of chitosan and chitosan-GLA microparticles as cost effective biosorbents for lead removal from wastewaters even at low levels.

References

1. CĂPĂŢÎNĂ, C., SIMONESCU, C.M., Environmental Engineering and Management Journal **7**(6), 2008, p. 717
2. BANCU, L., ŞTEFAN, S., JITARU, I., Rev. Chim. (Bucharest), **57**, no. 6, 2006, p. 582
3. PAULINO, A.T., SANTOS, L.B., NOZAKI, J., React. Funct. Polym., **68**, 2008, p. 634
4. DU, E.L., YU, S.M., ZUO, L.M., ZHANG, J.S., HUANG, X.Q., WANG, Y., Appl. Clay Sci. **5**, 2011, p. 94
5. NIU, Y., QU, R., SUN, C., WANG, C., CHEN, H., JI, C., ZHANG, Y., SHAO, X., BU, F., J. Hazard. Mater. **244-245**, 2013, p. 276
6. GHOLAMI, A., MOGHADASSI, A.R., HOSSEINI, S.M., SHABANI, S., F. GHOLAMI, F., Journal of Industrial and Engineering Chemistry, 2013, http://dx.doi.org/10/.1016/j.jiec.2013.07.041
7. MELINESCU A., TÂRDEI, C., SIMONESCU C.M., MARINESCU, V., MICLEA, A., Romanian Journal of Materials, **43** no. 2, 2013, p. 223
8. ALEXANDROAEI, M., IGNAT, M., SANDU, I.G., Rev. Chim. (Bucharest), **64**, no. 10, 2013, p. 1100

9. BULGARIU, L., ROBU, B., MACOVEANU, M., Rev. Chim. (Bucharest), **60**, no. 2, 2009, p. 171
10. HUBERT, K.N., BODOKI, E., DOUDOU, B.D., OPREAN, R., SANDULESCU, R., Rev. Chim. (Bucharest), **61**, no. 12, 2010, p. 1186
11. ŞTEFAN, D.S., BELCU, M., ŞTEFAN, M., MARINESCU, I.A., Rev. Chim. (Bucharest), **61**, no. 1, 2010, p. 31
12. HRISTODOR, C., COPCIA, V., LUTIC, D., POPOVICI, E., Rev. Chim. (Bucharest), **61**, no. 3, 2010, p. 285
13. HOSSEINI-BANDEGHARAEI, A., KARIMZADEH, M., SARWGHADI, M., HEYDARBEIGI, A., HOSSEINI, S.H., NEDAIE, M., SHOGHI, H., Chem. Eng. Res. Des., 2013, http://dx.doi.org/10.1016/j.cherd.2013.10.007
14. LIU, YX., YAN, JM., YUAN, DX., LI, QL., WU, XY., Chemical Engineering Journal, **218**, 15 2013, p. 81
15. ROJAS, R., Applied Clay Science, **87**, 2014, p. 254
16. SAHU, M.K., MANDAL, S., DASH, S.S., BADHAI, P., PATEL, R.K., Journal of Environmental Chemical Engineering, **1**, 4, 2013, p. 1315
17. LONG, Y., LEI, D., NI, J., REN, Z., CHEN, C., XU, H., Bioresource Technology, **152**, 2014, p. 457
18. PENG, X., XU, F., ZHANG, W., WANG, J., ZENG, C., NIU, M., CHMIELEWSKÁ, E., Colloids and Surfaces A: Physicochemical and Engineering Aspects, **443**, 2014, p. 27
19. MOHAN, D., KUMAR, H., SARSWAT, A., ALEXANDRE-FRANCO, M., PITTMAN Jr., C. U., Chemical Engineering Journal, **236**, 2014, p. 513
20. GAO, J., SUN, S.-P., ZHU, W.-P., CHUNG, T.-S., Journal of Membrane Science, **452**, 2014, p. 300
21. YUVARAJA, G., KRISHNAIAH, N., SUBBAIAH, M.V., KRISHNAIAH, A., Colloids and Surfaces B: Biointerfaces, **114**, 2014, p. 75
22. SIMONESCU, C.M., FERDEŞ, M., Polish Journal of Environmental Studies, **21**, no. 6, 2012, p. 1831
23. SIMONESCU, C.M., DELEANU, C., STANCU, M., CĂPĂŢÎNĂ, C., Journal of Environmental Protection and Ecology, **13** no 2, 2012, p. 462
24. SIMONESCU, C.M., DIMA, R., FERDEŞ, M., MEGHEA, A., Rev. Chim. (Bucharest), **63**, no. 2, 2012, p. 224
25. SIMONESCU, C.M., DINCĂ, O.-R., OPREA, O., CĂPĂŢÎNĂ, C., Rev. Chim. (Bucharest), **62** no. 2, 2011, 183
26. MARTÍNEZA,M., MIRALLES, N., HIDALGOA, S., FIOL, N., VILLAESCUSA, I., POCH, J., Journal of Hazardous Materials B133, 2006, p. 203
27. MARTÍN-LARA, M.A., RODRÍGUEZ, I.L., BLÁZQUEZ, G., CALERO, M., Desalination, **278**, 1–3, 1 2011, p. 132
28. TANG, Y., CHEN, L., WEI, X., YAO, Q., LI, T., Journal of Hazardous Materials, **244–245,** 2013, p. 603
29. LI, T.-T., LIU, Y.-G., PENG, Q.-Q., HU, X.-J., LIAO. T., WANG, H., LU, M., Chemical Engineering Journal, **214**, 2013, p. 189
30. BLÁZQUEZ, G., CALERO, M., RONDA, A., TENORIO, G., MARTÍN-LARA, M.A., J. Ind. Eng. Chem., 2013, http://dx.doi.org/10.1016/j.jiec.2013.11.003
31. NTHUMBI, R.M., NGILA, J.C., MOODLEY, B., KINDNESS, A., PETRIK, L., Physics and Chemistry of the Earth, Parts A/B/C, **50–52**, 2012, p. 243
32. DELEANU, C., SIMONESCU, C.M., CONSTANTINESCU, I., Rev. Chim. (Bucharest), **59**, no. 6, 2008, p 639
33. SIMONESCU, C.M., MARIN, I., ŢÂRDEI, C., MARINESCU, V., OPREA, O., CĂPĂŢÎNĂ, C., Rev. Chim. (Bucharest), **65**, no. 6, 2014, p. 627
34. CHOWDHURY S., SAHA, P., Chem. Eng. J. **164**, 2010, p. 168
35. NGAH, W.S.W., FATINATHAN, S., J. Environ. Sci. **22**(3), 2010, p. 338
36. TUNALI, S., ÇABUK, A., AKAR, T., Chem. Eng. J. **115**, 2006, p. 203
37. NGAH, W.S.W., FATINATHAN, S., Chem. Eng. J. **143**, 2008, p. 62
38. NGAH, W.S.W., ENDUD, C.S., MAYANAR, R., React. Funct. Polym. **50**, 2002, p. 625
39. KALYANI, G., BABU RAO, G., VIJAYA SARADHI, B., PRASANNA KUMAR Y., ARPN J. Eng. Appl. Sci. **4**(1), 2009, p.39
40. ZHANG, X., BAI, R.B., J. Colloid. Interf. Sci., **264**, 2003, p. 30

Manuscript received: 19.12.2013