

LEAD (II) REMOVAL FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO CHITOSAN

DOINA ASANDEI, LAURA BULGARIU and ELENA BOBU

*Faculty of Chemical Engineering and Environmental Protection,
"Gheorghe Asachi" Technical University,
700050 Iasi, Romania*

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The adsorption behaviour of lead (II) ions from aqueous solutions onto chitosan was investigated. Adsorption experiments were performed in a batch system, at room temperature (20 ± 0.5 °C), by changing the various experimental parameters: initial solution pH, chitosan dosage, initial lead (II) concentration and contact time. The results have shown that the effectiveness of lead ions removal is mainly dependent on the initial concentration of lead ions to chitosan dosage ratio, which should be optimized by a compromise between the removal yield and cost-effectiveness of the process. The adsorption equilibrium data were analyzed by the Freundlich and Langmuir isotherm models, whose application for the mathematical description of lead (II) adsorption on chitosan indicated that the adsorption equilibrium is well-fitted to the Langmuir isotherm.

Keywords: lead (II), chitosan, adsorption, removal yield, isotherms

INTRODUCTION

Aqueous pollution with heavy metals represents an important environmental problem, due to their toxic effect and accumulation tendency through food chains. Among heavy metals, lead (II) should be among the first to be removed from aqueous environments.¹⁻³ Environmental contamination induced by lead arises mainly *via* wastes from industrial processes, such as mining, extractive metallurgical processes, electroplating, pigments industries, etc.

The conventional methods for the removal of lead from waste waters include chemical precipitation, membrane separation, ion exchange adsorption and biosorption.⁴⁻⁸ However, many of them are expensive or have some disadvantages, such as incomplete removal of lead ions, low selectivity and high amount of toxic sludge, high cost and energy consumption.

Adsorption, an effective separation process for a wide variety of applications, is now reorganized as an effective and economical method for the removal

of pollutants from waste waters. The most widely used adsorbent is activated carbon,^{9,10} but it is quite expensive and, possibly, no cost-effective in the treatment of large waste water volumes. That is why, in the last years, considerable attention has been paid to low-cost biosorbents, as an alternative to reduce the cost of adsorption systems.

Many naturally occurring materials have been investigated for assessing their suitability in controlling water pollution. Peat,^{11,12} lignin,¹³ fungi^{14,15} are well known as low-cost biosorbents for removing lead (II) from aqueous solutions. Another interesting example of biosorbent is chitosan. Several studies have shown that chitosan is very efficient in removing various toxic and strategic metals, such as cadmium, mercury, molybdenum, uranium, vanadium, platinum and palladium.^{16,17}

Chitosan, a hydrophilic natural polymer produced by alkaline deacetylation of chitin, obtained mainly by extraction from shrimp and crab

shells, is the most abundant biopolymer occurring in nature, after cellulose.¹⁸ It is characterized by a high content of nitrogen, present as amine groups capable of adsorbing the metal ions through several mechanisms – including chemical interactions, such as chelation, electrostatic interactions or ion-exchange. The interaction type depends^{19,20} on the metal ion, its chemistry and initial solution pH.

The objective of the present investigation is to find out the optimum conditions for removing the lead (II) ions from aqueous solutions through adsorption on chitosan powder.

EXPERIMENTAL

Materials

The chitosan used in the study, purchased from *Vanson* ($M_w = 755900$, polydispersity index = 1.82, acetylating degree = 20.8%), was used without further purification. The chitosan sample was dried in air, for 6 h at 70 ± 3 °C in the oven, and then stored in a dessicator, for further use.

A stock solution of lead (II) ions, containing 2000 mg Pb(II)/L, was obtained by dissolving the lead nitrate (purchased from *Reactivul* - Bucharest) in twice-distilled water and standardized after preparation.²¹ All other concentration values, varying between 40 and 670 mg Pb(II)/L, were prepared by dilution from the stock solution. The initial pH of the working solution was obtained by adding small volumes of 0.5 N HNO₃ (for pH = 2.0 and 3.0), or acetate buffer (CH₃COOH/CH₃COONa), for $3.0 < \text{pH} < 6.0$.

Adsorption experiments

The batch experiments were performed by adding chitosan to a 25 mL solution containing lead (II) ions, under intermittent stirring, at room temperature (19 ± 0.5 °C) and, with the exception of only one series, at a constant contact time of 24 h. Four series of experiments were performed to evaluate the influence of the following variables: pH value of the initial solution, contact time, chitosan (adsorbent) dosage and initial concentration of the lead (II) solution. The influence of the initial solution pH on the lead (II) capacity of adsorption onto chitosan was investigated at two concentration levels of the lead (II) solution (84.53 and 169.07 mg Pb(II)/mL), over the 2.0-6.0 pH range, at a constant dosage of chitosan. To evaluate the effect of chitosan dosage on lead (II) adsorption, the lead (II) solution of a constant concentration (84.53 mg/L) was treated with variable dosages of chitosan (resulting in chitosan concentrations in the mixture from 5 to 40 g/L), at pH = 6.0 of the initial solution. The influence of the initial lead (II) concentration on chitosan adsorption

capacity was studied over the 40-670 mg Pb(II)/L concentration range, at pH = 6.0 of the initial solution and constant dosage of chitosan (5g/L concentration in the reaction volume). For each experiment, the phases were separated by filtration after the adsorption procedure and lead (II) concentration in aqueous solutions was analyzed spectrophotometrically with 4-(2-pyridilazo)-resorcinol (Digital Spectrophotometer S 104 D, $\lambda = 530$ nm, 1 cm glass cell),²² with a calibration graph.

Theoretical models

Two models – Langmuir and Freundlich – were used to describe the experimental adsorption isotherm.^{23,24}

The Langmuir isotherm equation may be formulated as

$$q = \frac{q_{\max} \cdot K_L \cdot c}{1 + K_L \cdot c} \quad (1)$$

The linearized form of the Langmuir equation after a rearrangement is

$$\frac{c}{q} = \frac{1}{q_0 \cdot K_L} + \frac{c}{q_0} \quad (2)$$

where: q_{\max} is the maximum adsorption ratio upon complete saturation of the chitosan surface; q is the current adsorption ratio, *i.e.* the amount of lead (II) ions retained per weight unit of adsorbent; K_L is the Langmuir constant related to the free energy of adsorption²³ and c is lead (II) concentration at equilibrium.

The Freundlich isotherm is an exponential equation that may be written as

$$q = K_F \cdot c^{1/n} \quad (3)$$

while the linear form is represented by the equation:

$$\lg q = \lg K_F + \frac{1}{n} \lg c \quad (4)$$

where: K_F is the Freundlich constant, indicating the adsorption capacity, n is a constant characterizing the affinity of the metal ion towards chitosan, q is the amount of lead (II) ions adsorbed per weight unit of chitosan and c is lead (II) concentration at equilibrium.

RESULTS AND DISCUSSION

Effects of process variables on lead (II) removal through adsorption on chitosan

Initial solution pH: The initial solution pH plays an important role in the adsorption of metal ions on various adsorbents, once it affects both the dissociation degree of the functional groups from the adsorbent surface and the speciation/solubility of the metal ions. In the study, the initial solution pH was varied between 2.0 and 6.0. According to

the lead speciation diagram,²⁵ over this pH domain, Pb (II) occurs predominantly as divalent free ions (Pb^{2+}), and the species can be involved in chemical processes during sorption on chitosan.

The graphs plotted in Figure 1 show the effect of the initial solution pH on Pb (II) adsorption onto chitosan, evaluated at two initial concentrations of Pb (II), and a constant dosage of chitosan (5 g/L), for a 24 h contact time. One can observe that the adsorption ratio (q , mg/g – amount of lead (II) adsorbed per weight unit of chitosan) increases with the initial pH, more markedly at higher initial Pb (II) concentration. The influence of the initial solution pH on the lead (II) adsorption ratio is explained by the ionic state of the functional groups from chitosan, involved in metal binding, as well as by the occurrence of the hydrated cation (Pb^{2+}), as a predominant ionic species. At low pH values, the adsorption ratio is low, due to the competition between the hydrogen and lead (II) ions for the adsorption sites of chitosan (dissociation of the –OH groups is strongly inhibited, while $-\text{NH}_2$ protonation determined electrostatic repulsions). By increasing the initial pH, the dissociation degree of the hydroxyl groups and the negative charge density on the chitosan surface, respectively, are increasing, resulting in a higher adsorption ratio by the electrostatic interaction with cations (Pb^{2+}). Based on these results, an initial solution pH of 6.0 (acetate buffer) was selected as the optimum value, for analyzing the influence of other parameters on lead (II) ions removal from aqueous solutions, through adsorption on chitosan powder.

Contact time: The influence of the contact time between adsorbent (chitosan) and the lead (II) aqueous solution was analysed under the following conditions: initial solution concentration – 169.07 mg Pb (II)/L, pH = 6.0 (acetate buffer), and chitosan dosage = 5 g/L. The results presented in Figure 2 evidence a steep increase in the adsorption ratio (q , mg/g) in the first 20 min of the contact time, when an adsorption yield of 96.55% is attained. The equilibrium state is practically obtained after 80 min and the adsorption ratio reaches the same level as for a 24 h contact time (Fig. 1).

According to Qin *et al.*,²⁶ the fast initial adsorption could be the result of a very high transfer rate of the metal ions to the surface of adsorbent particles, while the slow adsorption in the

second step is a consequence of the low diffusion rate of metal ions into the intra-particles pores of the adsorbent.

Chitosan dosage: In Figure 3, the removal yield (R , %) and adsorption ratio (q , mg/g) of the lead (II) ions are plotted as a function of the chitosan dosage. The experiments were performed at a constant initial Pb (II) concentration of 84.53 mg/L, pH = 6.0, for a contact time of 24 h. The yield of Pb (II) removal increases from 64.09 to 97.99%, while the adsorption ratio decreases from 10.76 to 2.07 mg/g with the chitosan dosage. These opposite effects could be attributed to the increasing number of possible binding sites at high dosages of chitosan, producing a reduction of the adsorption surface and leading to a saturation point, when no further lead (II) adsorption occurs.²⁷ One may observe that the maximum adsorption ratio appears at the lowest chitosan concentrations, while a higher removal yield requires increasing dosages of chitosan. However, chitosan dosages over 20g/L do not change significantly the level of removal yield, becoming no cost-effective.

Initial lead (II) concentration: Figure 4 illustrates the effect of initial lead (II) concentration (c_0 , mg/L) on the adsorption ratio and removal yield of Pb (II) onto chitosan powder. In this experiment, the following parameters were kept constant: initial solution pH = 6.0 (acetate buffer), chitosan dosage corresponding to a 5 g/L concentration, contact time – 24 h. At a constant dosage of 5g/L chitosan and under equilibrium conditions (24 h contact time), the adsorption ratio (q , mg/g) increases and retention yield (R , %) decreases slowly for a Pb (II) concentration of up to 250 mg/L, and very fast after this level of initial concentration (Fig. 4). These effects could be explained by the fact that, at a high metal ion concentration, the available superficial groups of chitosan are already occupied and, consequently, the diffusion of lead (II) ions on the unreacted functional groups is inhibited.

The influence of the different conditions on the adsorption rate and removal yield of lead (II) ions on chitosan powder evidenced that process effectiveness is mainly dependent on the ratio of the initial concentration of lead ions to chitosan concentration (dosage). Generally, at pH = 6.0 and a contact time of 80 min or higher, the increase in the initial concentration of lead ions requires an increase in the chitosan dosage.

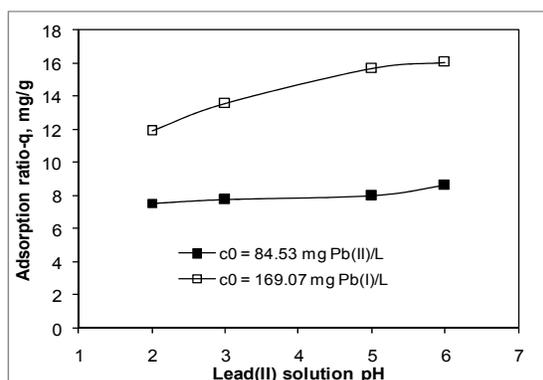


Figure 1: Adsorption ratio of Pb (II) onto chitosan as a function of initial solution pH

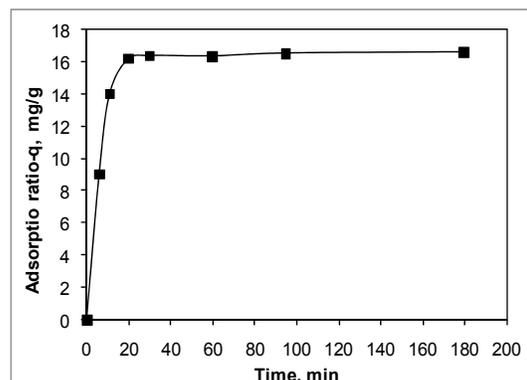


Figure 2: Adsorption ratio of lead (II) onto chitosan as a function of contact time

Adsorption isotherm – Langmuir and Freundlich mathematical models

The adsorption isotherm, representing the equilibrium distribution of the lead (II) ions between the solid phase of adsorbent and the aqueous solution, obtained in the case of lead (II) adsorption onto chitosan, is presented in Figure 5. Equilibrium adsorption experiments have been performed under experimental conditions, demonstrating the maximum adsorption capacity of chitosan for lead (II) ions (pH = 6.0 – acetate buffer; chitosan dosage – 5 g/L; temperature = 20 °C; contact time = 24 h).

The Langmuir and Freundlich linear models were used for the mathematical description of adsorption (Figs. 6 and 7). The values of the characteristic parameters (n , K_F , q_0 and K_L), calculated from the intercept and slope of linear dependencies, and the correlation coefficients (R^2) associated to each model (Freundlich and Langmuir isotherms) are summarized in Table 1.

The values of the correlation coefficients (R^2) indicate that lead (II) adsorption onto chitosan is very well described by the Langmuir isotherm model ($R^2 = 0.9980$), although a good correlation coefficient ($R^2 = 0.9340$) may be also provided by the Freundlich isotherm model. These results permit the supposition that a monolayer adsorption of lead (II) on chitosan occurs, with the observation that the adsorption sites from the chitosan surface are heterogeneous. This means that, when lead (II) is adsorbed on the surface, different sorption sites had different affinity for lead (II) ions and different adsorption energy. Constant (n) from the Freundlich model, which estimates the adsorption intensity of the metal ion on the adsorbent surface is higher than 1, suggesting that favourable adsorption occurs even at high Pb (II) concentrations. On the other hand, the high value of the Langmuir constant (K_L), which characterizes the binding energy of adsorption, confirms the chemical nature of lead (II) adsorption on chitosan.

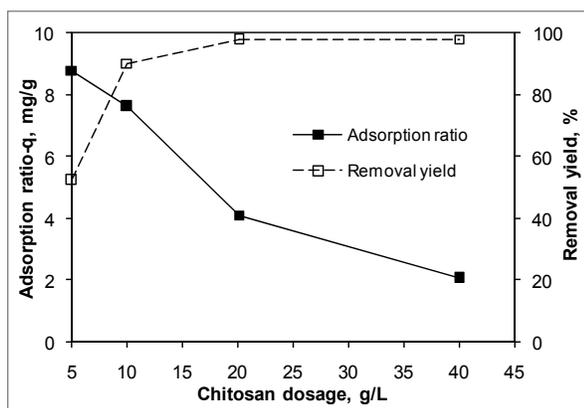


Figure 3: Adsorption ratio and removal yield of Pb (II) onto chitosan as a function of chitosan dosage

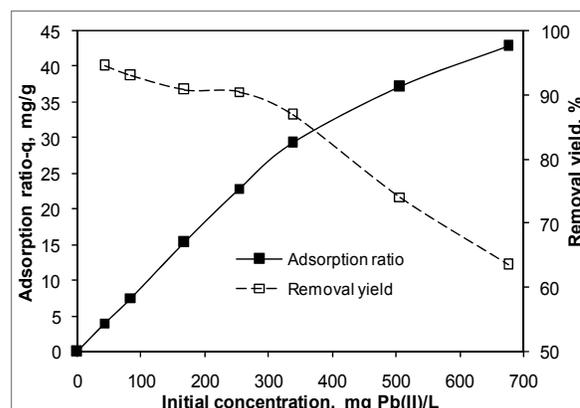


Figure 4: Adsorption ratio and removal yield of Pb (II) onto chitosan as a function of initial concentration in Pb (II) solution

In the same case, maximum adsorption (q_{\max}), which is a measure of the adsorption capacity to form a monolayer, presents a high value and sustains the hypothesis that strong interactions

occur between the functional groups of the adsorbent and the lead (II) species of the aqueous solutions.

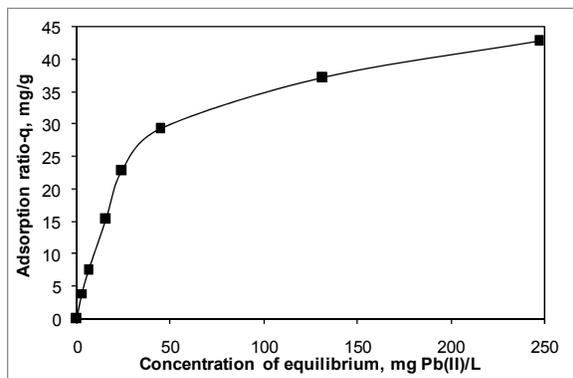


Figure 5: Adsorption isotherm of lead (II) on chitosan powder

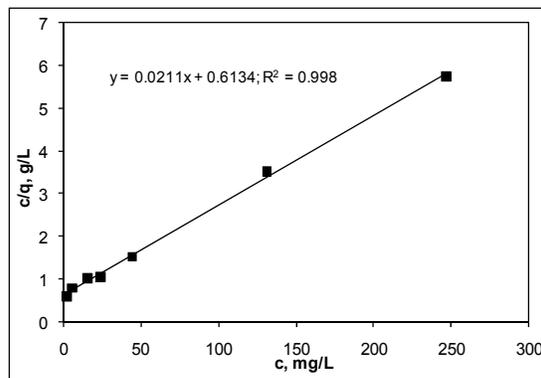


Figure 6: Linear model of Langmuir isotherm for lead (II) adsorption onto chitosan

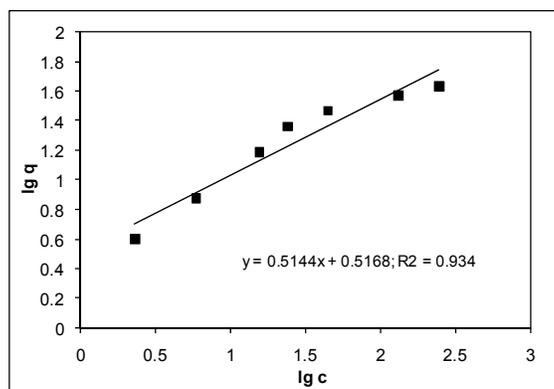


Figure 7: Linear model of Freundlich isotherm for lead (II) adsorption onto chitosan

Table 1
Isotherm characteristic parameters for lead (II) adsorption onto chitosan

Parameter	Langmuir model	Freundlich model
Equation	$y = 0.0211x + 0.6134$	$y = 0.5144x + 0.5168$
R^2	0.9980	0.9340
n	-	1.9440
$K_F, \text{mg L}^{1/n}/\text{g mg}^{1/n}$	-	3.2870
$q_{\max}, \text{mg/g}$	47.3933	-
$K_L, \text{L/mg}$	0.0343	-
$\Delta G, \text{kJ/mol}$	- 21.6138	-

The change in the free Gibbs energy (ΔG) was calculated from the Langmuir constant using equation $-\Delta G = -RT \ln K_L$ (where R is the universal gas constant (8.314 J/mol K) and T is the absolute

temperature). The negative value of ΔG (Table 1) indicates that the adsorption process of lead (II) onto chitosan is feasible and spontaneous.

CONCLUSIONS

The adsorption of lead (II) from aqueous solutions onto chitosan was investigated. The experiments were performed in batch system, at room temperature (20 ± 0.5 °C), on analysing the effects of the following variables: initial solution pH, contact time, chitosan dosage and initial lead (II) concentration. The results lead to the following conclusions:

- The adsorption ratio of lead (II) on chitosan increases by changing the pH from acid towards neutral, while the optimum pH value for lead (II) removal was found to be 6.0 (acetate buffer);
- The equilibrium state of the interaction between lead ions and the chitosan surface is reached after an 80-min contact time, when the adsorption ratio level is the same as for a 24h contact time;
- The removal yield of lead (II) increases slightly with the chitosan dosage, while the adsorption rate (mg Pb(II)/g chitosan) significantly decreases, and thus, at a chitosan dosage higher than 20 g/L, the process is not cost-effective;
- The adsorption ratio of lead (II) on chitosan increases with the initial metal ion concentration of up to 670 mg/L, while a relatively high removal yield ($R > 90\%$) is attained only for initial concentrations below 250 mg/L;
- Process effectiveness is mainly dependent on the ratio of initial concentration of the lead ions to chitosan concentration (dosage), which has to be optimized by a compromise between the removal yield and the process cost-effectiveness.

The application of the Langmuir and Freundlich isotherm models for the mathematical description of lead (II) adsorption onto chitosan permits the following conclusions:

- Adsorption equilibrium data are very well fitted to the Langmuir isotherm, the maximum adsorption rate (q_{\max}) – of 47.39 mg/g – occurring under the experimental conditions studied;
- The value of the free Gibbs energy (ΔG), calculated from the Langmuir constant, is negative, indicating that the adsorption process of lead (II) onto chitosan is feasible.

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