

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

G. GYANANATH and D. K. BALHAL

School of Life Sciences, S. R. T. M. University, Nanded, India

Received August 11, 2011

The adsorption of Pb (II) ions onto chitosan beads and cross-linked chitosan beads has been investigated. The epichlorohydrin (ECH) was used as a cross-linking agent. Experiments were carried out as a function of pH, stirring time, adsorbent dosage and concentration of Pb (II) ions. The experimental data of the adsorption equilibrium from Pb (II) solution correlated well with the Langmuir isotherm equation. The uptake of Pb (II) ions on chitosan beads was of 72.89 mg Pb (II)/g chitosan, while on ECH cross-linked chitosan beads, it was of 39.42 mg Pb (II)/g chitosan.

Keywords: chitosan beads, cross-linked chitosan beads, adsorption, metals

INTRODUCTION

The presence of heavy metal ions, such as Pb, Cr, Zn, Cu, Cd and Ni, in the environment has become of great concern because of their constantly increasing discharge by a number of industries, toxicity to the environment and other adverse effects on receiving waters. For example, Pb is highly toxic to humans, causing mental deficiency, brain damage, anaemia, as well as behavioural problems.

Several methods for removing toxic metal ions are known, such as ion exchange, filtration reverse osmosis, adsorption, complexation, precipitation and electrode deposition.¹ However, since these treatment methods are not cost-effective, numerous low adsorbent materials have been developed for the removal of toxic metal ions.²

Chitin, poly (1, 4)-2-acetamido-2-deoxy- β -D-glucan is a value-added biopolymer extracted commercially from the shells of crustaceans, such as prawns, crabs and shrimps, being the second most abundant biopolymer next to cellulose.³ Chitin is used to obtain chitosan, a well-known adsorbent for transition metal ions, which has the tendency to form complexes with them, allowing the recovery of transition metal ions from solution. An acid environment contributes to the partial dissolution of the polymer; therefore, to make it insoluble in an acidic medium, it should

be modified by using cross-linking agents. Although cross-linking reduces the adsorption capacity, it enhances the resistance of chitosan against acids, alkali and chemicals.⁴ The cross-linked chitosan is very stable and maintains its strength even in acidic and basic solutions.⁵ These characteristics are very important for an adsorbent, so that it could be used in a lower pH environment. Thus, the present study aims to compare the effectiveness of chitosan beads and cross-linked chitosan beads for the removal of Pb (II) ions from solution under simulated conditions.

EXPERIMENTAL

Materials

The chitosan used in the study was purchased from Sigma Aldrich. Epichlorohydrin (ECH) and nitrate purchased from Sd. Fine Mumbai were of analytical grade. Chitosan beads and ECH cross-linked chitosan beads were prepared according to the procedure described by Wan Ngah *et al.*⁶

Preparation of chitosan beads

Chitosan solution was prepared by dissolving 2 g of chitosan in 60 mL of 5% (v/v) acetic acid solution. The chitosan solution was sprayed into a precipitation bath containing 500 mL of 0.50 M NaOH, which neutralized the acetic acid within the chitosan gel beads. A magnetic stirrer was used to stir the aqueous

NaOH solution. The wet chitosan gel beads were extensively rinsed with distilled water to remove any NaOH, filtered and finally air dried to remove the water from the pore structure (hereafter called chitosan beads). The beads were ground and sieved to a constant size (<250 μm) before use.

Preparation of cross-linked chitosan beads

A solution of 0.10 M epichlorohydrin containing 0.067 M NaOH was prepared (pH 10). Freshly prepared wet chitosan beads were added to the epichlorohydrin solution to obtain a ratio of 1:1 with chitosan (mol ECH: mol CH_2OH). The chitosan beads in epichlorohydrin were heated to a temperature between 40 $^\circ\text{C}$ and 50 $^\circ\text{C}$ for 2 hours and stirred continuously using a magnetic stirrer. After 2 hours, the beads were filtered and washed intensively with distilled water to remove any unreacted epichlorohydrin, then filtered and air dried. The newly formed beads (hereafter called chitosan cross-linked beads) were ground and sieved to a constant size (<250 μm) before use.

Adsorption experiments

A stock solution of lead (Pb) ions of 1000 mg/L was prepared by dissolving the lead nitrate in distilled water. This stock solution was then diluted to obtain different concentrations (100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/L).

Batch adsorption experiments were performed in a 250 mL beaker and equilibrated using a magnetic stirrer. Then, 100 mL aliquots of these standard solutions were equilibrated with 5 g/L chitosan or cross-linked chitosan beads. After filtration, the concentration of Pb (II) in the supernatant was analysed by using an Atomic Absorption spectrophotometer (Perkin Elmer 100). The effect of Pb adsorption was studied in the pH range of 2-6. The pH of the initial solution was adjusted to a pH value using 0.1 M HNO_3 and 0.1 M NaOH. Chitosan and cross-linked chitosan beads were equilibrated at a particular pH for about 80 min and at 200 mg/L initial Pb (II) concentration. The effect of the agitation

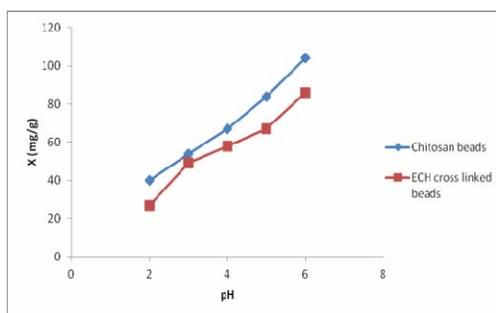


Figure 1: Effect of pH on Pb adsorption onto chitosan beads and cross-linked chitosan beads

period, adsorbent dosage and Pb (II) ion concentration was also studied to determine the optimum conditions for adsorption of Pb (II) ions.

Adsorption equilibrium studies were carried out using a constant time of 80 min at pH 6.0 for both types of beads. Isotherm studies were conducted with constant chitosan and cross-linked chitosan beads (5 g/L) and varying the initial concentration of Pb (II) in the range 100-1000 mg/L. The adsorption capacity was calculated based on the difference of Pb (II) concentration in an aqueous solution (100 mL) and the weight of the beads (5 g/L) as given below:

$$\text{Adsorption capacity (X)} = (C_0 - C_e) V/W \quad (1)$$

where C_0 is the initial Pb concentration (mg/L), C_e is the final or equilibrium Pb concentration (mg/L), V is the volume of Pb solution (mL) and W is the weight of the chitosan or cross-linked chitosan beads (g).

RESULTS AND DISCUSSION

Effect of pH

Fig. 1 shows the effect of pH on the adsorption of Pb (II) by chitosan beads and cross-linked chitosan beads. The adsorption increases with an increasing pH of the solution. This could be explained by the fact that at a low pH, the amine groups in the beads were easily protonated, which induced electrostatic repulsion of Pb (II) ions. Therefore, there existed a competition between protons and Pb (II) ions for adsorption sites, and as a result, the adsorption capacity decreased. At a higher pH, the degree of dissociation of the $-\text{OH}$ groups and the negative charge density on the chitosan surface, respectively, resulted in a higher adsorption by the electrostatic interaction with cation Pb^{2+} for both types of beads.

Effect of stirring

The influence of lead in relation to the contact time between adsorbent and Pb (II) aqueous solution was analysed.

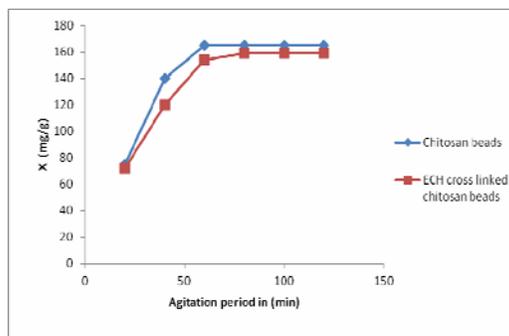


Figure 2: Effect of stirring time on adsorption of Pb onto chitosan beads and ECH cross-linked chitosan beads

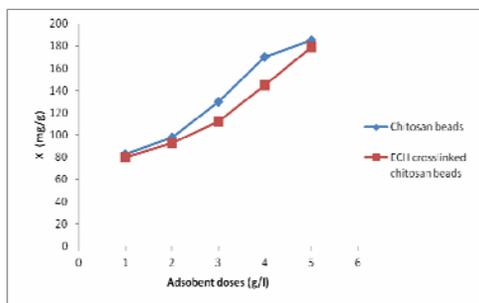


Figure 3: Effect of adsorbent dose on adsorption of Pb onto chitosan beads and ECH cross-linked chitosan beads

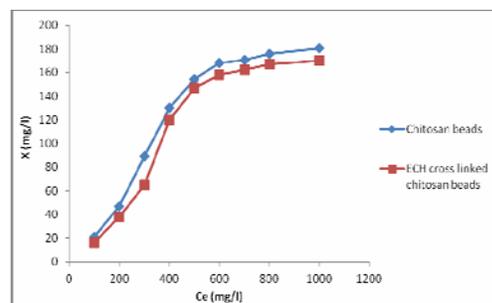


Figure 4: Adsorption isotherm of Pb onto chitosan beads and ECH cross-linked chitosan beads

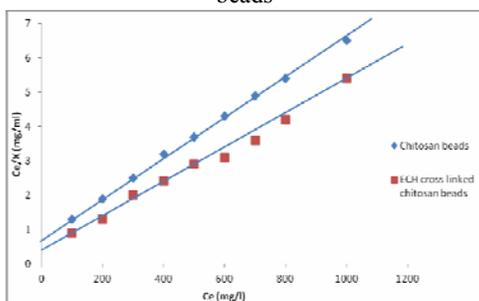


Figure 5: Linear model of Langmuir isotherm for Pb (II) adsorption onto chitosan beads and cross-linked chitosan beads

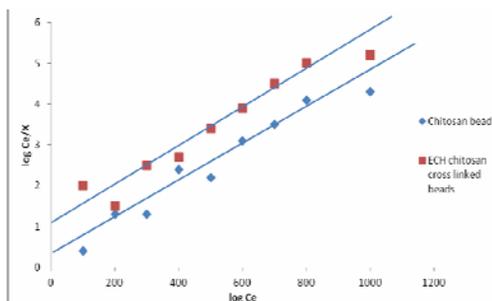


Figure 6: Linear model of Freundlich isotherm for Pb (II) adsorption onto chitosan beads and cross-linked chitosan beads

Fig. 2 shows that adsorption of Pb (II) increased with stirring time and equilibrium was achieved at about 80 min for chitosan beads and 90 min for ECH cross-linked chitosan beads at a concentration of 200 mg/L.

Effect of adsorbent dosage

Fig. 3 plots the adsorption of Pb (II) ions onto chitosan beads and ECH cross-linked chitosan beads at different doses of the adsorbent. The adsorption of Pb (II) onto both types of beads increased, which is due to the increasing number of possible binding sites at a high dosage of adsorbent, producing the reduction of the adsorption surface and leading to a saturation point, when no further Pb (II) adsorption occurs. However, an adsorbent dosage over 5 g/L does not change significantly the level of removal of lead (II) for chitosan beads and cross-linked chitosan beads.

Adsorption isotherms

Fig. 4 presents the equilibrium isotherm for the adsorption of Pb (II) onto chitosan beads and ECH cross-linked chitosan beads. Their

adsorption behaviours can be described with the Langmuir and Freundlich adsorption equations.

Langmuir equation is given as:

$$C_e/X = C_e/X_{\max} + 1/X_{\max} b \quad (2)$$

where C_e is the equilibrium or final concentration Pb (II) (mg/L), X is the amount of Pb (II) adsorbed per weight unit of chitosan beads or cross-linked chitosan beads at equilibrium concentration (mg/g), X_{\max} is the maximum adsorption at monolayer coverage (mg/g) and b is the Langmuir adsorption equilibrium constant (mL/mg) and is a measure of the energy of adsorption.

Freundlich equation is given as:

$$\ln X = \ln K_f + 1/n \ln C_e \quad (3)$$

Where K_f (mg/g) is the Freundlich constant, n is the constant characterizing the affinity of the metal ions towards chitosan beads, X (mg/g) is the amount of lead ions adsorbed per weight unit of chitosan beads and C_e (mg/L) is the equilibrium concentration.

The values of the characteristic parameters (n , K_f , X and b) calculated from the intercept and slope of linear dependencies and the correlation

coefficient (R^2) associated to each model (Freundlich and Langmuir isotherms) are summarized in Table 1.

The values of the correlation coefficient (R^2) indicate that lead (II) adsorption onto chitosan beads and ECH cross-linked chitosan beads is described very well by the Langmuir isotherm model, compared to the Freundlich isotherm model. The correlation coefficient calculated from

the Langmuir isotherm for chitosan beads is $R^2 = 0.9993$ and for ECH cross-linked beads – $R^2 = 0.9955$. These results indicate that maximum adsorption (X_{max}), which is the measure of the adsorption capacity to form a monolayer, presents a high value and supports the hypothesis that strong interactions occur between the functional groups of the adsorbent and the lead (II) species of the aqueous solutions (Elena Bobu *et al.*)⁷.

Table 1
Experimental Langmuir and Freundlich isotherm constants

Adsorbents	Langmuir			Freundlich		
	X_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
Chitosan beads	72.89	349.83	0.9993	21.32	10.33	0.9756
ECH cross-linked chitosan beads	39.42	534.02	0.9955	9.07	16.56	0.9708

CONCLUSIONS

The adsorption of lead (II) from aqueous solutions onto chitosan beads and ECH cross-linked chitosan beads was investigated. The results obtained in the study under experimental conditions led to conclusions below.

- The adsorption of lead onto chitosan beads and ECH cross-linked chitosan beads increased by changing the pH from acid towards neutral, while the optimum pH value for lead removal by both types of beads was found to be 6.0.
- The equilibrium state of the interaction between lead ions and the surface of chitosan beads is reached after 80 min, while for ECH cross-linked beads, equilibrium is reached after 90 min of stirring, when the adsorption level is the same as for 24 h stirring time.
- The removal of lead by chitosan beads and ECH cross-linked chitosan beads increases with an increase in the adsorption dosage, while there was no significant increase in lead adsorption by both types of beads at a bead concentration higher than 5 g/L.
- Adsorption equilibrium data are fitted much better to the Langmuir isotherm, compared to

the Freundlich isotherm model. The maximum adsorption rate, X_{max} , for chitosan beads was of 72.89 mg/g and for ECH cross-linked chitosan beads, was of 39.42 mg/g, under experimental conditions. Although chitosan beads present a higher adsorption capacity than that of cross-linked chitosan beads, cross-linked chitosan beads have the advantage that they can be used in a low pH (acidic) solution, where chitosan beads dissolve.

REFERENCES

- ¹ C. S. Brooks, "Metal Recovery from Industrial Wastes", Lewis Publishers, Chelsea, MI, 1991.
- ² S. E. Bailey, T. J. Olin, R. M. Bricka and D. D. Adrian, *Water Res.*, **33**, 2469 (1999).
- ³ R. A. A. Muzzarelli, "Chitin", Pergamon Press, Oxford, 1977, p. 1114.
- ⁴ K. Inoue, Y. Baba Yoshizuka, *Bull. Chem. Soc. Jpn.*, **66**, 2915 (1993).
- ⁵ X. Zeng and E. Ruckenstein, *J. Membrane Sci.*, **148**, 195 (1998).
- ⁶ W. S. Wan Ngah, C. S. Endud and R. Mayanar, *React. Funct. Polym.*, **50**, 181 (2002).
- ⁷ Elena Bobu, D. Asandei and L. Bulgariu, *Cellulose Chem. Technol.*, **43(4-6)**, 211-216 (2009).