

Removal of Heavy Metal (Pb⁺²) From Lead (II) Nitrate Solution by Using Chitosan Bead

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Abstract

Chitosan is a derivation of chitin, which is the second most abundant natural polymer after the cellulose. In this research work, chitosan bead was prepared and it was used as biosorbent. Batch adsorption experiments were performed at five different initial heavy metal ion concentration (20,40,60,80,100 mg/L), and pH of solutions ranging from 4 to 6. Results showed that pH 5 was the most suitable. The percentage metal removal approached equilibrium within 60 min for lead and chitosan bead can remove (Pb²⁺) from lead (II) nitrate solution until 99.97 percent. So, chitosan bead can be used as biosorbent for treatment of waste water.

Keywords: chitosan, lead II nitrate, biosorbent, chitosan bead

Introduction

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 (Mohamad Jaafar & Abdul Sukor, A. S. (2021). Chitosan obtains from chitin. It is 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.

Chitosan is natural linear polysaccharides comparing of glucosamine and N-acetyl glucosamine and can be obtained by the partial deacetylation of chitin Carlos Roberto Bellato, (2010). Nowadays, chitosan is used in versatile applications. In the vastly diverse fields ranging from waste management to food processing, medicine and biotechnology, the uses of chitosan are widely. It becomes an interesting material in pharmaceutical applications because of its capability as biodegradability and biocompatibility, and low toxicity. Chitosan based hydrogel beads have been successfully used for the removal of metal ions, dyes, phenols, various amines, pesticides and fungicides by adsorption. The Chitosan beads have an ability as high swelling capacity which is significantly. The freeze-dried chitosan beads appear as solid white particles and have an average size of 3.5 ± 0.4 mm.

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 the other adverse effects on receiving waters. For example, lead is one of the toxic heavy metals that not only accumulate in individual but also have the ability to affect the entire food chain and disrupt the health system of human beings such as mental deficiency, brain damage and also animals and phytoplankton. The present study aims to reduce toxic heavy metal, lead ion concentration by using prepared biosorbent bead.

Materials and Method

Sampling and general experimental techniques

Sample Collection

The chitosan used in the study was purchased from Hlaing Thar Yar Industrial Zone, Yangon. All samples were cut into small pieces and dried in air and good ventilation place.

Determination of Physiochemical Properties of Commercial Chitosan Flake

Some physiochemical properties of the commercial chitosan such as moisture content, ash content, pH, bulk density and degree of deacetylation were determined. Moisture content and ash content of the commercial chitosan were determined by oven drying method (AOAC,2000). pH was determined by pH meter. Bulk density was measured by using bulk density bottle. The degree of deacetylation of (DDA) of chitosan sample was examined by hydrogen chloride titrimetric method. The resulting data are summarized in Table 1.

Determination of Degree of Deacetylation Content of Chitosan

Chitosan (2g) was completely dissolved in 200mL of freshly prepared 0.2M HCl solution and 100mL of concentrated hydrochloric acid was then added to the homogenous chitosan solution with vigorous stirring to precipitate the hydrochloride salt. The result solution was centrifuged for 15min and the supernatant was described.

The chitosan hydrochloride salt was then filtered off and washed several times with methanol until filtrate was neutral to litmus. Residual moisture in the chitosan hydrochloride salt was removed by stirring for 6hr in acetone. After final filtration, the precipitate was dried in a vacuum desiccator for 12hr to yield white chitosan hydrochloride salt.

The resulted chitosan hydrochloride salt was divided into two portions, one portion was placed in oven at 100°C to determine moisture content. In the other portion, an accurately weighted chitosan hydrochloride salt was dissolved in distilled water and the volume made up 100mL in the volumetric flask. The resulting solution (25mL) was titrated against a standard 0.05M sodium hydroxide solution using phenolphthalein as an indicator.

Preparation of Chitosan Beads

Chitosan solution was prepared by dissolving 5g of chitosan powder in 200mL of 1% acetic acid solution with constant stirring at room temperature for 3 hours. After stirring, the solution was left to stay overnight. Then, the solution was dropped into 5% NaOH solution with disposal Syringe (0.5 mm diameter). The chitosan drops coagulated in the NaOH solution and give spherical beads. After 24hours of contact with NaOH solution, beads were removed and rinsed several times with distilled water until pH do not change. The beads were dried at room temperature and collected in air tight container.

Measurement Solubility of Chitosan and Chitosan Beads

Solubility of chitosan and chitosan beads were examined by various solvents. 1.0g of each sample was weighed and put into a test tube following by adding 100mL of 1%(v/v) acetic acid solution. The suspensions were mixed and allowed to hydrate for 3hours at room temperature. The physical appearance was observed and recorded in Table2. Similarly, the solubility of each sample in other solvents was determined as the same procedure.

Adsorption experiment

A stock solution of lead (Pb) ions of 100mg/L was prepared by dissolving the lead nitrate in distilled water. This stock solution was then diluted to obtain different concentrations (20,40,60,80 and 100 mg/L).

Batch adsorption experiments were performed in a 250mL beaker and equilibrated using a magnetic stirrer. Then, 20mL aliquots of these standard solutions were equilibrated with 5g/L chitosan beads. After filtration, the concentration of Pb (II) in the supernatant was analyzed by using an Atomic Adsorption Spectrophotometer. The effect of Pb adsorption was studied in the pH range of (4.6). The pH of the initial solution was adjusted to a pH value using 0.1M HCl and 0.1M NaOH solution. Chitosan beads were equilibrated at a particular pH for about 60min and at 100 mg/L initial Pb (II) concentration. The effect of the agitation period, adsorbent dosage and Pb (II) ion concentration was also studied to determine the optimum conditions for adsorption of Pb (II) ions.

Results and Discussion

Results of Physicochemical properties of Commercial Chitosan Flake

Physicochemical properties of commercial chitosan flake were determined and the results are shown in Table 1.

Table 1. Results of Physicochemical properties of Commercial Chitosan Flake

No.	Properties	Parameter
		Chitosan Flake
1	Moisture (%)	2.50
2	pH	6.00
3	Ash (%)	9.02
4	Bulk Density (lb ft ⁻³)	28.97
5	Degree of Deacetylation (%)	68.08

According to these data, the moisture content of commercial chitosan flake was found to be 2.5%. Chitosan is hygroscopic in nature so it is very possible that the commercial sample was effective by moisture adsorption during storage. [Khan, T., et al., 2002]. Ash content of demineralization resulted in products having 31-36% ash. Some residual ash of chitosan may affect their solubility. [Bough, W.A., Satter, BIE. (1978)]. The bulk density of chitosan was found to be 28.97lbft⁻³. This may be due to the particle size and porosity of the material before treatment. [Rout, S.K., (2001)]. The degree of deacetylation was found to be 68.08% for commercial chitosan flake.

Comparison of Solubility of Chitosan Flake and Chitosan Bead

Solubility of chitosan flake and chitosan bead were compared and the results are shown in Table 2.

Table 2. Results of Solubility of Chitosan Flake and Chitosan Bead

Solvent	Solubility	
	Chitosan flake	Chitosan bead
Dilute Acetic acid	+	-
Hydrochloric acid	±	-
Sulphuric acid	-	-
Ethanol	-	-
Methanol	-	-
Sodium Hydroxide	-	-

(+) soluble, (±) partially soluble, (-) insoluble

The solubility tests were carried out using some organic solvent at room temperature. It is insoluble in alkali and organic solvent. It does not dissolve in sulphuric acid because it found chitosan sulphate which is a white crystalline solid. Hydrochloric acid required heating and stirring for hours. It is soluble in acetic acid. More rigid non cross link chitosan bead is insoluble in all type of solution.

Effect of pH

The initial solution pH plays an important role in the adsorption of metal ions on various adsorbents. In the study, the initial solution pH was varied between 4 to 6. According to the lead speciation diagram, over this pH domain, Pb (II) occurs predominantly as divalent free ions (Pb^{2+}), and the species can be involved in chemical process during sorption on chitosan bead. The graphs plotted in Figure (1) shows the effect of pH and a constant dosage of chitosan 0.5 g/100 ml for a 60 min contact time.

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 are strongly inhibited, while -NH₂ protonation determined electrostatic repulsions). By increasing the initial pH, the dissociation degree of the hydroxyl groups and the negative charge density on respectively, are increasing resulting in a higher adsorption ratio by the electrostatic interaction with cations (Pb^{2+}). Based on these results, the initial solution pH of 5 was selected as the optimum value, for analyzing the influence of the other parameters on lead (II) ions removal from aqueous solutions.

Table 3. Effect of pH on the Removal of Pb²⁺ Ion

Initial concentration (mg/L)	percent removal of Pb (II) ion		
	pH-4	pH-5	pH-6
20	99.97	99.97	99.97
40	99.97	99.97	99.97
60	97.30	99.97	99.97
80	77.40	97.56	95.18
100	76.96	88.09	83.85

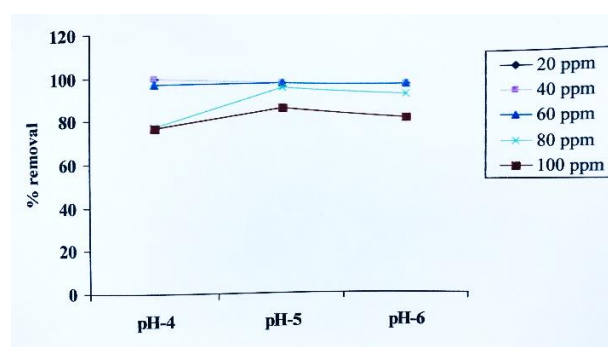


Figure 1. Effect of pH on the removal of Pb²⁺ ion

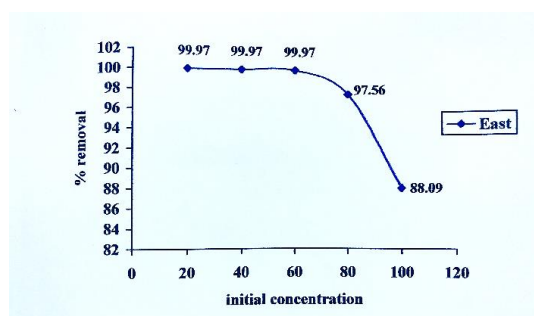


Figure 2. Effect of metal ion concentration

Figure (2) illustrates the effect of initial lead (II) concentration (C_0 , mg/L) on the adsorption ratio and removal percent of Pb (II) onto chitosan bead. In this experiment, the following parameters were kept constant: the pH of initial solution-5, contact time-60 min, adsorbent dosage = 0.5g / 100mL. At a constant dosage of 0.5g chitosan bead and under equilibrium conditions, percent removal decreases very fast after 80 ppm of initial concentration. Therefore, the increase in the initial concentration of lead ions requires on increase in the chitosan dosage.

Conclusion

In this study, chitosan bead has been evaluated as possible biosorbent for removal of lead from aqueous lead nitrate solution.

The chitosan sample was used as precursor material in preparation of chitosan bead. The characterization and solubility test for raw chitosan were carried out.

In addition, the removal of the toxic heavy metal ion (Pb^{2+}) on chitosan bead is investigated. The results of the investigation have shown that the metal removal percent depends on pH and the initial concentration of metal ion. The optimal pH for the removal of Pb^{2+} ion was observed at 5. The maximum percent removal Pb^{2+} ion by chitosan bead was found to be 99.97 % at initial metal ion concentration 20-60 ppm.

Consequently, the modified chitosan bead is a suitable adsorbent for removal of lead ion from waste water effluent in terms of low cost, natural and valuable alternatives for commercial sorbents.

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