ADSORPTION OF COPPER (II) IONS ONTO CHITOSAN AND CROSS-LINKED CHITOSAN BEADS

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ABSTRACT

The adsorption of Cu (II) ions onto chitosan and cross-linked chitosan beads has been investigated. Three different cross-linking agents were used to do the modification and the agents were gluteraldehyde (GLA), epichlorohydrin (ECH) and ethylene glycol diglycidyl ether (EGDE). Experiments were carried out as a function of pH, agitation period, agitation rate and concentration of Cu (II) ions. A pH of 6.0 was found to be a optimum for copper adsorption on chitosan and cross-linked chitosan beads. Isotherm studies indicate that heavy metals such as copper can be effectively removed by chitosan and cross-linked chitosan beads. Adsorption isothermal data could well interpreted by the Langmuir equation. Langmuir constants have been determined for chitosan and cross-linked chitosan beads. The experimental data of the adsorption equilibrium from Cu (II) solution correlated well with Langmuir isotherm equation. The uptake of Cu (II) ions on chitosan beads were 80.71 mg Cu (II)/g chitosan, chitosan-GLA beads were 59.67 mg Cu(II)/g Chitosan-GLA, chitosan-ECH beads were 62.47 mg Cu(II)/g chitosan-ECH and chitosan-EGDE beads were 45.94 mg Cu(II)/g chitosan-EGDE. The Cu (II) ions can be removed from the chitosan and cross-linked chitosan beads rapidly by treatment with an aqueous EDTA solution and at the same time the chitosan and cross-linked chitosan beads can be regenerated and also can be used again to adsorb heavy metal ions.

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

INTRODUCTION

The presence of heavy metals in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effect on receiving waters. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production, fertilizer industry, etc (1). Excessive intake of copper results in an accumulation in the liver. It is also toxic to aquatic organisms even at very small concentration in natural water (1).

Various methods exist for the removal of toxic metals from aqueous solution such as ion exchange, reverse osmosis, adsorption, complexion and precipitation (2-4). Adsorption is the most effective and widely used method. Activated carbon and chelation ion exchange resins have become increasingly popular compared to other techniques. In spite of its large use in the water and waste industries, activated carbon and commercial chelating resins are still an expensive material and therefore the production of its low-cost alternatives has been the focus of researchers in the area.

Biosorption or sorption to material of biological origin is recognized as an emerging technique for the treatment of wastewater containing heavy metals. Chitosan is a biopolymer, which gains it interest among researchers concerning the adsorption of metal ions on chitosan. Chitosan, also named poly(β-1-4)-2-amino-2-deoxy-D-glucopyranose, a poly(D-glucosamine) is prepared from chitin by deacetylating its acetamido groups. Chitin or poly((β-1-4)-2-acetamido-2-deoxy-D-glucopyranose is a natural polymer extracted from crustacean shells, such as prawns, crabs, insects and shrimps. Chitosan has been described as a suitable natural polymer for the collection of metals ions (5-14), since the amine groups and hydroxyl groups on the chitosan chain can act as chelation sites for metal ions. Acid environments produce the partial dissolution of the polymer and to make the polymer insoluble in acidic medium, modification by using cross-linking agents used. Although cross-linking reduces the adsorption capacity but it enhance the resistance of chitosan against acid, alkali and chemical (15). The cross-linked chitosan also are very stable and maintain their strength even in acidic and basic solutions (16). These characteristics are very important for a adsorbent so that it can be used in a lower pH environment. Cross-linking also can change the crystalline nature of chitosan and enhance the sorption abilities (17).

The aim of this study was to compare the adsorption behaviour of chitosan and cross-linked chitosan beads. The equilibria of adsorption of Cu(II) ion on these beads from water were investigated. The influence of experimental conditions such as agitation period, agitation rate, pH and Cu(II) ions concentration will be studied. This information will be useful for further application in treatment of waste effluents.

EXPERIMENTAL

Chemical and Reagents

Chitosan was purchased from Fluka BioChemika as a flaked material, with a deacetylation percentage of approximately 57.72 % (defined by IR method). Gluteraldehyde (GLA), epichlorohydrin (ECH), and ethylene glycol diglycidyl ether (EGDE) purchased from Fluka Chemika with analytical reagent grade. All the reagents used were of analytical reagent grade. Doubly distilled water used to prepare all the solutions.

Preparation of Chitosan Beads

Chitosan solution was prepared by dissolving 2.00 g chitosan flakes into 50 mL of 5 % (v/v) acetic acid solution. The solution was sprayed into a precipitation bath containing 250 mL of 0.50 M NaOH, which neutralized the acetic acid within the chitosan gel and thereby coagulated the chitosan gel to a spherical uniform chitosan gel beads. The aqueous NaOH solution was stirred using magnetic stirrer. 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 then ground by using a laboratory jar mill and sieved to a constant size (< 250 μm) before use.

Preparation of Cross-linked Chitosan Beads

Three different cross-linking agents used to modify chitosan at a ratio of 1:1 (chitosan: cross-linking agent).

(a) Gluteraldehyde

A recently prepared wet chitosan beads (as described before) were suspended in gluteraldehyde solution 0.05 M to obtain a ratio of 1:1 with chitosan. The chitosan beads in resulting gluteraldehyde solution were left standing for 24 hours at room temperature. After 24 hours the cross-linked chitosan beads were intensively washed with distilled water, filtered and air-dried. The newly formed beads (hereafter called chitosan-GLA beads) were ground to a constant particle size (< 250 μm) before use. The chitosan-GLA beads obtained were confirmed by a Perkin-Elmer FTIR System 2000 model spectrometer.

(b) Epichlorohydrin (ECH)A solution of 0.010 M epichlorohydrin containing 0.067 M sodium hydroxide was prepared (pH 10). Freshly prepared wet chitosan beads were added to this epichlorohydrin solution to obtain a ratio of 1:1 with chitosan. The chitosan beads in epichlorohydrin were heated to a temperature between 40-50 °C for 2 hours and stirred continuously. After 2 hours the beads were filtered and washed intensively with distilled water to remove any unreacted epichlorohydrin and air-dried. The newly formed cross-linked beads (hereafter called chitosan-ECH beads) were ground to a constant size (< 250 μm) before use. The chitosan-ECH beads obtained were confirmed by a Perkin-Elmer FTIR system 2000 model spectrometer.

(c) Ethylene glycol diglycidyl ether (EGDE)

Chitosan beads were prepared as mentioned earlier. A solution containing 5 % (v/v) EGDE prepared and added to the wet chitosan beads with a 1:1 stoichiometric ratio between amino functions and ether groups. The resulting solution were heated to a temperature 50-60° C for 3 hours and stirred continuously. After 3 hours, the newly cross-linked chitosan beads were intensively washed and air-dried. The beads (hereafter called chitosan-EGDE beads) were ground to a constant particle size (< 250 μm) before use. The chitosan-EGDE beads obtained were confirmed by a Perkin-Elmer FTIR system 2000 model spectrometer.

Dissolution and Swelling Test of Chitosan and Cross-linked Chitosan Beads

Chitosan and cross-linked chitosan beads were tested with regard to their solubility in each of 5 % (v/v) acetic acid, distilled water and 0.10 M sodium hydroxide solution by adding 0.10 g of chitosan and cross-linked chitosan beads in each of the dilute acid, distilled water and dilute alkaline solutions for a period of 24 hours with stirring.

The swelling studies of chitosan and cross-linked chitosan beads were carried out in distilled water at room temperature for a period of 24 hours. The percentage of swelling of these beads were calculated by using the following equation:

$$\text{Percentage of swelling} = \frac{W_s - W_d}{W_d} \times 100\ \% \qquad (1)$$

where W_s is the weights of swollen beads and W_d is the weights of dry beads.

Adsorption Experiments

Stock solution (1000 ppm) of Cu(II) was used in this study. This stock solution was then diluted to give standard solution of 5 ppm. Batch adsorption experiments were conducted in 250 mL beaker and equilibrated using a magnetic stirrer. Then 100 mL aliquots of these standard solutions were placed in 250 mL beakers and equilibrated with 0.010 g of chitosan or cross-linked chitosan beads. After filtration, the concentration of Cu(II) in supernatant was analyzed using atomic absorption spectrophotometer (Instrumental Laboratory ILAAS 357 model). The effect of Cu(II) adsorption was studied in the pH range of about 1-6. The pH of the initial solution was adjusted to the pH value using 0.10 M HNO_3 or 0.10 M NaOH. Chitosan and cross-linked chitosan beads were equilibrated at the particular pH for about 30 minutes and at an initial Cu(II) concentration of 5 ppm. The effect of agitation period and agitation rate also studied to determined the optimum condition for adsorption of Cu(II) ions.

Adsorption equilibrium studies were conducted using a contact time of 60 minutes at pH 6.0 for chitosan, chitosan-GLA and chitosan-ECH beads whereas for chitosan-EGDE beads, a contact time of 90 minutes at pH 6.0. Isotherm studies were conducted with a constant chitosan and cross-linked chitosan beads weight (0.010 g) and varying initial concentration of Cu(II) in the range 0-14 ppm. The amount of adsorption was calculated based on the difference of Cu(II) concentration in aqueous before and after adsorption, the volume of aqueous solution (100 mL) and the weight of the beads (0.010 g) according to:

$$\text{Adsorption capacity (X)} = \frac{(C_o - C_e)V}{W} \qquad (2)$$

where C_o is the initial concentration of Cu(II) (ppm). C_e is the final or equilibrium Cu(II) concentration (ppm), V is the volume (mL) Cu(II) solution, and W is the weight (g) of the chitosan or cross-linked chitosan beads.

For desorption studies, 0.010 g of chitosan and cross-linked chitosan beads were loaded with Cu(II) using 100 mL of 5 ppm Cu(II) solution at optimum pH and an agitation period of 60 minutes was given for chitosan, chitosan-ECH and Chitosan-GLA beads and 90 minutes for chitosan-EGDE beads. The agitation rate was fixed at 500 rpm for all the beads. Cu(II)-loaded chitosan and cross-linked beads were collected, gently washed with distilled water to remove any unabsorbed Cu(II). The amount of Cu(II) adsorbed per gram of chitosan and cross-linked chitosan beads were determined by using the supernatant Cu(II) concentration. The chitosan and cross-linked chitosan beads were agitated with 100 mL of EDTA of various concentrations (10^{-2} - 10^{-6} M) and the amount of desorbed Cu(II) was determined as before.

RESULTS AND DISCUSSION

Solubility and Swelling Test of Chitosan and Cross-linked Chitosan Beads

It shows that after cross-linking, chitosan insoluble in acidic and alkaline medium so as distilled water (Table1). The swelling behaviour of chitosan also improved after cross-linking. These two characteristics are very important so that, the chitosan beads can be used in low pH value as can be seen, chitosan can be dissolved in 5 % (v/v) acetic acid while the cross-linked chitosan beads were not. Meanwhile, the less swelling behaviour of cross-linked chitosan beads was important so that it can be used in an adsorption column. The percentage of swelling of chitosan and cross-linked chitosan beads were given below in Table 2.

Table 1. Solubility effect of chitosan and cross-linking chitosan beads

	Solubility effect		
Beads	5 % (v/v) Acetic acid	Distilled water	0.10 M NaOH
Chitosan	Soluble	Insoluble	Insoluble
Chitosan-GLA	Insoluble	Insoluble	Insoluble
Chitosan-ECH	Insoluble	Insoluble	Insoluble
Chitosan-EGDE	Insoluble	Insoluble	Insoluble

Table 2. Swelling behaviour of chitosan and cross-linked chitosan beads

	Percentage of swelling (%)		
Beads	5 % (v/v) Acetic acid	Distilled water	0.10 M NaOH
Chitosan	Soluble	39.8	35.9
Chitosan-GLA	15.6	11.9	9.5
Chitosan-ECH	20.6	17.5	13.6
Chitosan-EGDE	14.1	6.2	4.5

Effect of pH

Fig. 1 shows the effect of pH on the adsorption of Cu(II) by chitosan and cross-linked chitosan beads. The maximum adsorption of Cu(II) on chitosan and cross-linked chitosan beads was fixed at pH 6.0. From Fig. 1, a knowledge of pH is important in this study because of the dependence of the percentage adsorption of Cu(II) on pH. The adsorption increases (i.e. the change of absorbance increases) with increasing the pH. pH is the major parameter which greatly influences the maximum uptake. At the low pH, competition between proton and Cu(II) ions causes a low uptake capacity. The optimum pH is related to a lower pH than the value required for the precipitation of metal ions (9). This is because of the formation of Cu(II) hydroxides after pH 6.0 and it shows that most of the Cu(II) ions removed by the precipitation of Cu(II) ions with hydroxide ions. Therefore pH 6.0 is chosen as maximum pH to avoid formation of Cu(II) hydroxide which will affect the adsorption. Chitosan beads show chelating ability towards a number of metal ions because of its amine groups and hydroxyl groups that can act as electron donors (18). The nitrogen electron present in the amine groups can establish dative bonds with transition metal ions. The presence of second interaction of copper with hydroxyl groups of carbon 3 is expected to (19). Chitosan beads were soluble at low pH value, cross-linked chitosan beads were not soluble at low pH. This is due to the less free amine groups and hydroxyl groups in the cross-linked chitosan beads that contribute to the low solubility in acidic medium.

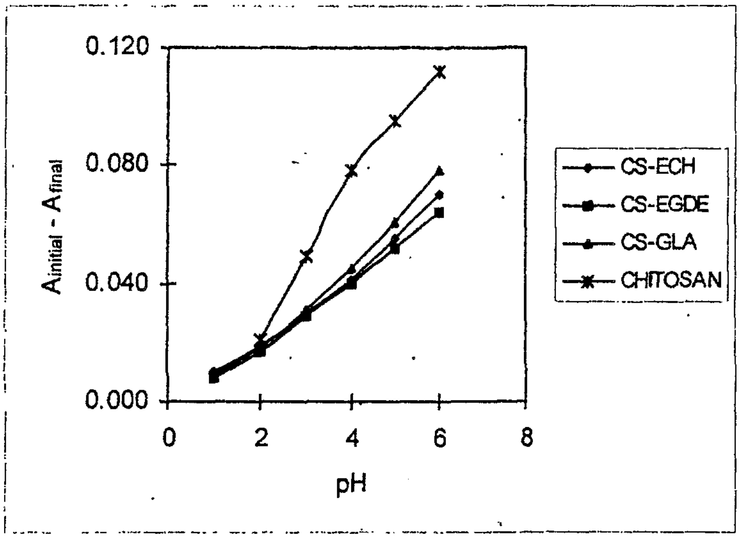

Fig. 1. Effect of pH for the Cu^{2+} adsorption on chitosan and cross-linked chitosan beads: A, absorbance

Effect of Agitation Period

The optimum period for the adsorption of Cu(II) on chitosan and cross-linked chitosan beads can be observed by looking at the final absorbance of Cu(II) solution after adding chitosan and cross-linked chitosan beads. Fig. 2 shows the effect of agitation period on the adsorption of Cu(II) by chitosan and cross-linked chitosan beads. The adsorption of Cu(II) increases with agitation period and attains equilibrium at about 60 minute for chitosan, chitosan-GLA and chitosan-ECH beads, and 90 minutes for chitosan-EGDE beads for an initial Cu(II) concentration of 5 ppm. It shows that the adsorption of Cu(II) remains constant after 60 minutes for chitosan, chitosan-GLA and chitosan-ECH beads and 90 minutes for chitosan-EGDE beads, implying that equilibrium has been reached. Therefore the optimum agitation period for adsorption of Cu(II) were about 60 minutes for chitosan, chitosan-GLA and chitosan-ECH beads, and 90 minutes for chitosan-EGDE beads.

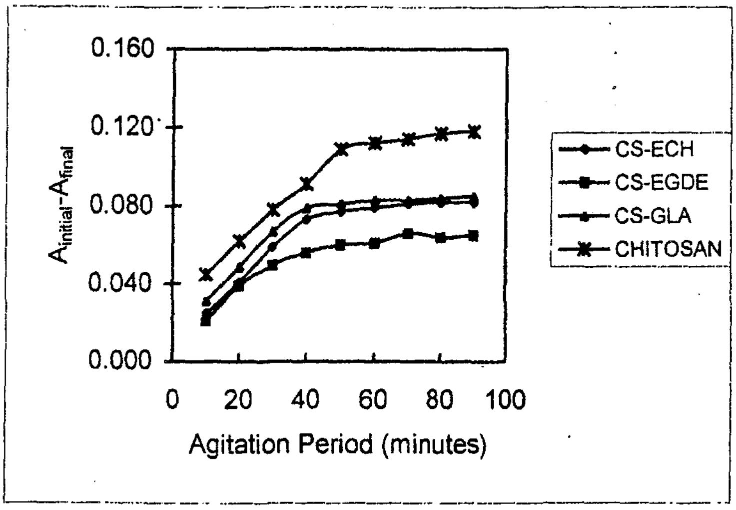

Fig. 2. Effect of agitation period for the adsorption of Cu^{2+} on chitosan and cross-linked chitosan beads

Effect of Agitation Rate

Fig. 3 shows the effect of agitation rate on the adsorption of Cu(II) by chitosan and cross-linked chitosan beads. The adsorption of Cu(II) increases with agitation rate and attains a constant value at about 500 rpm for all the beads. Therefore the optimum agitation rate for adsorption of Cu(II) were 500 rpm for chitosan and cross-linked chitosan beads.

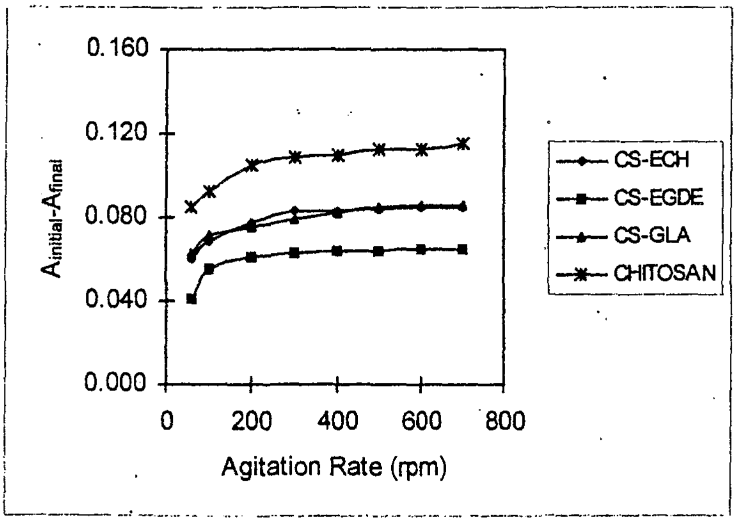

Fig. 3. Effect of agitation rate for the adsorption of Cu^{2+} on chitosan and cross-linked chitosan beads

Adsorption Isotherms

Fig. 4 shows the experimental equilibrium isotherms for adsorption of Cu(II) on chitosan, chitosan-GLA, chitosan-ECH and chitosan-EGDE beads. From the figures, we can do a assumption that adsorption of Cu(II) on chitosan and cross-linked chitosan beads take place only to a certain amount.

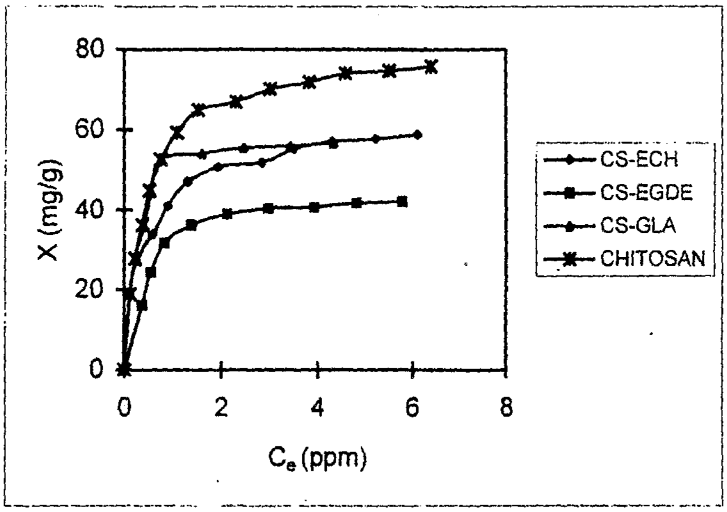

Fig. 4. Adsorption isotherms of Cu^{2+} on chitosan and cross-linked chitosan beads

The adsorption characteristic of adsorbate onto adsorbent can be characterized by using the Langmuir model. By rearranging the general equation, a linear form is given as below:

$$\frac{C_e}{X} = \frac{C_e}{X_{max}} + \frac{1}{X_{max}b} \qquad (3)$$

where C_e is the equilibrium or final concentration of Cu(II) (ppm), X is the amount of Cu(II) adsorbed per unit weight of chitosan 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 adsorption equilibrium constant (mL/mg) and is measure of energy of adsorption. Fig. 5 shows the relation between C_e and C_e/X for chitosan and cross-linked chitosan beads. It shows the experimental adsorption isotherm values fitted into the linearized forms of Langmuir equation. The linear plots show that adsorption obeys Langmuir isotherm model for both chitosan and cross-linked chitosan beads. From the slope and intercept of Langmuir isotherm, the numerical values of Langmuir isotherm constants were summarized in Table 3.

Table 3. Experimental Langmuir isotherm constants

Beads	Adsorption constant	
	X_{max} (mg/g)	b (mL/mg)
Chitosan	80.71	2.40
Chitosan-GLA	59.67	4.84
Chitosan-ECH	62.47	2.27
Chitosan-EGDE	45.62	2.16

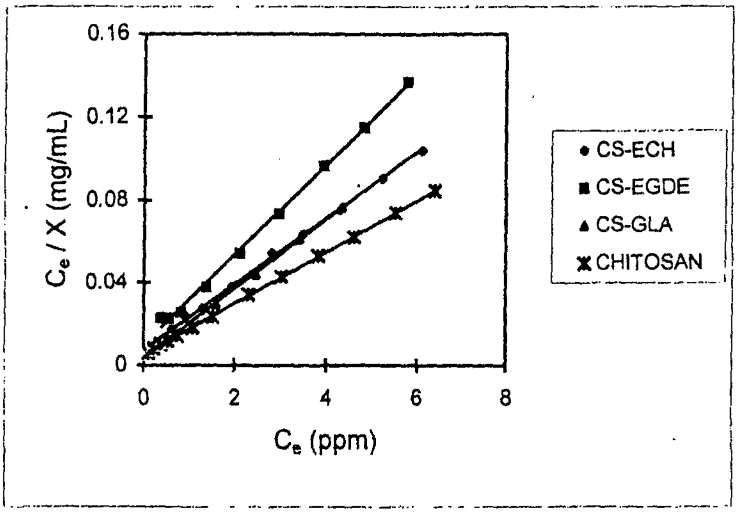

Fig. 5. Adsorption isotherms of Cu^{2+} on CS-ECH, CS-EGDE, CS-GLA and chitosan beads, linearized according to the Langmuir equation

It has been reported that the effect of isotherm shape with a view to predicting if an adsorption system is 'favourable' or 'unfavourable' (20). The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by (21):

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where C_o is the initial Cu(II) concentration (ppm), and b is Langmuir's constant adsorption equilibrium constant (mL/mg). The parameter indicates the isotherm shape according to Table 4.

Table 4. Effect of separation factor on isotherm shape

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The value of R_L for different initial Cu(II) concentration for chitosan and cross-linked chitosan beads are given in Table 5. The R_L values show that favourable adsorption of Cu(II) on chitosan and cross-linked chitosan beads takes place, therefore chitosan and cross-linked chitosan beads are favourable adsorbers.

Table 5. R_L values based on the Langmuir equation

Cu(II) initial concentration (ppm)	R_L values			
	Chitosan	Chitosan-GLA	Chitosan-ECH	Chitosan-EGDE
2	0.172	0.094	0.180	0.188
4	0.094	0.049	0.099	0.104
6	0.065	0.033	0.068	0.072
8	0.050	0.025	0.082	0.055
10	0.040	0.020	0.042	0.044

Chitosan and cross-linked chitosan beads can be considered to be microporous biopolymers; therefore pores are large enough to let Cu(II) ions through. The mechanism of ions adsorption on porous adsorbents mainly follows three steps (22):

(i) diffusion of ions to the external surface of adsorbent.
(ii) diffusion of ions into the pores of adsorbent.
(iii) adsorption of the ions on the internal surface of adsorbent.

The first step of adsorption may be affected by metal ion concentration, agitation period and rate. The last step of the adsorption is considered as a rate-determining step and as a relatively rapid process.

Desorption Studies

Desorption studies will help to elucidate the nature of adsorption process and to recover the Cu(II) from chitosan and cross-linked chitosan beads. Moreover, it also will help to regenerate the chitosan beads so that it can be used again to adsorb metal ions. EDTA is used to do the desorption studies. Chitoson beads were soluble in higher concentration of EDTA solution and only low concentration can be used. Whereas, cross-linked chitosan beads were not soluble in EDTA solution although at higher concentration. Percentage of desorption of Cu(II) from chitosan and cross-linked chitosan beads by using EDTA are listed in Table 6.

Table 6. Percentage of desorption of Cu(II) from complex Cu(II)-chitosan and cross-linked chitosan beads

Concentration of EDTA (M)	Percentage of desorption (%)			
	Chitosan	Chitosan-GLA	Chitosan-ECH	Chitosan-EGDE
1.0×10^{-2}	-	95.38	97.67	82.30
1.0×10^{-3}	-	86.82	92.54	63.03
1.0×10^{-4}	65.24	84.55	71.09	44.21
1.0×10^{-5}	34.31	34.40	22.22	21.90
1.0×10^{-6}	5.88	10.61	7.01	13.54

CONCLUSION

Chitosan and cross-linked chitosan beads can be an effective adsorbents for collection of Cu(II) ions from aqueous solution. Although chitosan beads show higher adsorption capacity than cross-linked chitosan beads but cross-linked chitosan beads can be used in low pH solution and its also show lower percentage of swelling. These two characters are essential for an adsorbent so that it can be used as a resin in ion exchange chromatography columns. Moreover, cross-linked chitosan beads show better desorption results at higher concentration of EDTA, whereas chitosan beads soluble in higher concentration of EDTA. Therefore, cross-linked chitosan beads can be regenerated well compare to chitosan beads and can be used again to adsorb metal ions.

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