

Removal of Copper(II) and Nickel(II) Using Binary Biopolymer Bead

B. MAHALAKSHMI DEVI¹, THANDAPANI GOMATHI² and P.N. SUDHA^{2,*}

¹Department of Chemistry, Bharathiar University, Coimbatore-641 046, India

²P.G and Research Department of Chemistry, D.K.M. College for Women, Vellore-632 001, India

*Corresponding author: E-mail: drparsu8@gmail.com

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This study aims to synthesize chitosan (CS)/sodium alginate (SA) binary bead for removal of the heavy metals such as copper and nickel from the synthetic wastewater solution. The binary bead of weight ratio 1:1 was prepared in the presence of glutaraldehyde crosslinker and characterized using FTIR and XRD analysis for analyze its formation and adsorption suitability. Batch adsorption study was preferred to determine the adsorption efficiency of the binary bead by varying the parameters such as pH, adsorption time, adsorption dose and initial metal ion concentration. The results revealed that the prepared binary bead acts as the good adsorbent even at the low metal ion concentration. The participation of the biopolymers such as chitosan and alginate in the copper and nickel removal process were examined by fitting the experimental data in the isotherm and kinetics studies. The isotherm and the kinetics study results showed that multilayer adsorption had taken place following the pseudo-second order kinetics.

Keywords: Chitosan/sodium alginate binary bead, Crosslinking, Adsorption isotherm, Batch adsorption study.

INTRODUCTION

The pollution due to heavy metals is a problem prevailing worldwide and the influence of heavy metal pollution on the human health is very serious [1,2]. Industrial effluents from various factories are rich in various heavy metals which include not only the common metals such as sodium, calcium, strontium, but also toxic metals such as arsenic, chromium, cadmium, mercury, nickel, copper zinc, lead, vanadium and titanium, *etc.* [3]. When present beyond the acceptable limits the heavy metals become toxic and also carcinogenic [4]. The high solubility of the heavy metals in water make it available in various forms in aquatic environment such as colloidal, particulate and dissolved phases [5]. This occurrence in water bodies may be either of natural origin or of anthropogenic origin [6]. These heavy metals show toxicity by way of forming stable complexes with natural materials such as proteins in the organisms, in which groups such as carboxylic acid (-COOH), amine (-NH₂) and thiol (-SH) are involved. The modified molecules in the biological organisms lose their ability to function properly which may lead to cell degradation or cell death.

Nowadays, there are a wide variety of different methods in practice for the efficient removal of heavy metal from waters. Some of the more prominent ones are coagulation, flocculation, chemical precipitation, ion exchange, ultrafiltration, adsorption,

ion-exchange, reverse osmosis, oxidation, ozonation, membrane filtration processes, sonication [7] and electrochemical technologies [4]. But adsorption plays a vital role in wastewater treatment.

The marine polysaccharide chitosan is a biopolymer which is an excellent biosorbent for the removal of heavy metal ions due to its (1) high hydrophilicity, (2) presence of high number of different functional groups such as acetamido, primary amino and/or hydroxyl group), (3) chitosan is highly reactive and (4) the structure of the polymer chain is highly flexible [8]. Also, as chitosan acts as a cation in the acidic medium that is the amino group is protonated which makes the exchange of metal ions by chitosan through adsorption process [9,10]. Thus in the present study the biopolymer chitosan was chosen as the basic material. To enhance the adsorption property of chitosan, another biopolymer alginate was blended with it and prepared in the bead form.

Sodium alginate is totally non-toxic and it has the property of formation of viscous solutions and gels. Thus sodium alginate is becoming more widespread used in the food industry as a thickening agent, in biotechnology as an immobilization matrix, in medicine and agriculture for controlled release of drugs and pesticides and in wastewater treatment. The cross-linking of the chains of α -L-gulonate blocks through the divalent cations such as Ca²⁺ leads to the electronegative cavities capable of holding the cations *via* ionic interactions,

resulting in into a structure resembling an “egg box” [11]. As the crosslinked alginates have the ability to form very stable structures, they have been used for the removal of heavy metal from wastewater [12,13]. Though alginates derived from algae are capable of sequestering heavy metals through carboxyl groups [14,15], there are very few studies which show the use of alginates as biosorbent for the removal of heavy metals from aqueous solutions.

Hence the study was aimed to prepare the novel binary beads using the promising biopolymers such as chitosan and alginate in the presence of crosslinker for the removal of heavy metals copper and nickel from aqueous solution. The prepared beads were characterized using FTIR and XRD for its formation and suitability. The adsorption studies were done through batch adsorption mode by varying the parameters such as adsorbent dose, contact time, pH and initial metal ion concentration.

EXPERIMENTAL

Chitosan was obtained from Indian sea foods, Cochin, Kerala. Sodium alginate was obtained from Nice Chemicals Private Ltd. The crosslinking agent glutaraldehyde was obtained from SD-fine-chemicals Limited, India. All the reagents used to prepare the solutions were of analytical reagent grade.

Preparation of chitosan/sodium alginate beads: Chitosan/sodium alginate binary beads of ratio 1:1 were prepared in the presence of crosslinker glutaraldehyde through ionic cross-linking method. Initially the chitosan solution was prepared by dissolving 1 g of chitosan in 25–30 mL of 2 % acetic acid solution. Then this solution was blended with sodium alginate (2 g in 30 mL water) under stirring over a period of 15 min. The stirring process was continued until a uniform dispersion was obtained. The resultant homogeneous dispersion was then dropped through a syringe needle into 100 mL of 2 % calcium chloride. The beads of chitosan/sodium alginate were allowed to stand in calcium chloride solution for 24 h and after 24 h, it was then washed and dried. The crosslinked chitosan/sodium alginate bead was prepared by dipping the dried beads in glutaraldehyde solution for 24 h. It was then finally washed with distilled water and dried.

FTIR studies: The prepared chitosan/sodium alginate bead was characterized by FTIR spectroscopy. Measurements were performed on these samples with a Perkin Elmer 200 FT-IR spectrophotometer using potassium bromide pellets. The FTIR spectra were obtained in the wave number range from 4000 to 450 cm^{-1} .

X-ray diffraction (XRD) studies: The X-ray diffraction patterns of the samples were tested by an X-ray scattering SHIMADUZ XD-diffractometer using in filter $\text{CuK}\alpha$ radiation source ($\lambda = 0.154 \text{ nm}$), set a scan rate = 10/min, using a voltage of 40 kv and a current of 30 mA.

Batch adsorption studies: Batch adsorption experiment was performed at room temperature for the removal of Cu(II) and Ni(II) ions from aqueous solution using chitosan/sodium alginate (1:1) bead prepared in the presence of glutaraldehyde, as a function of various parameters such as by changing the adsorbent dose, pH of the solution and time of shaking of the

adsorbent metal solution mixture. Initially a standard solution (200 mg/L) of copper(II) and nickel(II) ion were prepared separately in 1000 mL double distilled water. For each experimental run, about 1 g of chitosan/sodium alginate bead (adsorbent) was added to 100 mL of metal solution (200 mg/L). The mixture was agitated well using orbit shaker at a speed of 160 rpm for 1 h at room temperature. The adsorbent was removed by filtration and the filtrate was tested for the quantity of copper using atomic absorption spectrophotometer (AAS analysis).

The percentage removal of Ni(II) and Cu(II) ion was determined by following equation:

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100$$

where C_o = initial concentration of nickel and copper (mg/L); C_e = Cu(II) concentration remaining in solution (mg/L).

RESULTS AND DISCUSSION

FTIR studies: The FTIR spectrum of chitosan and chitosan/sodium alginate bead was shown in Fig. 1(a) and Fig. 1(b). The FTIR spectrum of chitosan shows the peaks at 3454, 2923, 1628, 1540, 1421, 1384 cm^{-1} , etc. A broad peak obtained at 3454 cm^{-1} indicates the OH and NH stretching. A strong peak observed at 1628, 1540, 1421 and 1384 cm^{-1} shows the presence of carbonyl stretching, NH_2 bending, OH bending and CN stretching respectively. Whereas for chitosan/sodium alginate bead the prominent peaks appeared at 3426, 2919, 1604 and 1381 cm^{-1} corresponds to the –OH and –NH group, CH stretching, C=O stretching and OH bending vibration respectively.

From the comparison of FT-IR results of chitosan/alginate bead with pure chitosan it was evident that the shift in the vibrational frequencies (3454 cm^{-1}) corresponding to OH stretching and NH stretching in pure chitosan to lower vibrational frequency ranges (3426 cm^{-1}) in chitosan/sodium alginate beads was observed. This observed information suggests that the NH and OH groups were involved in intermolecular hydrogen bonding effectively. When compared to pure chitosan, the intensity of the peak around 1540 cm^{-1} attributed to the presence of NH bending gets decreased in the case of chitosan/sodium alginate bead.

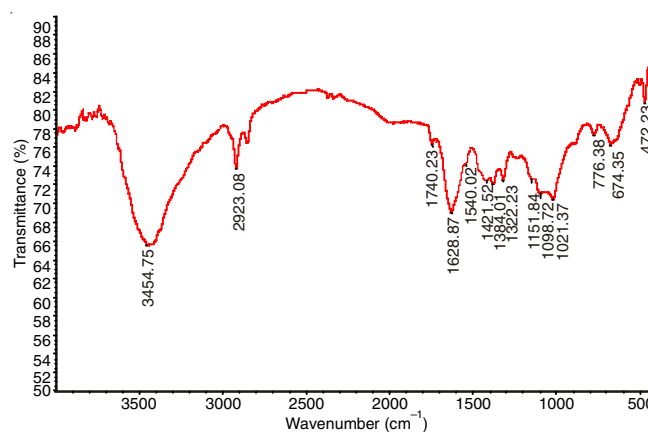


Fig. 1a. FTIR spectrum of chitosan

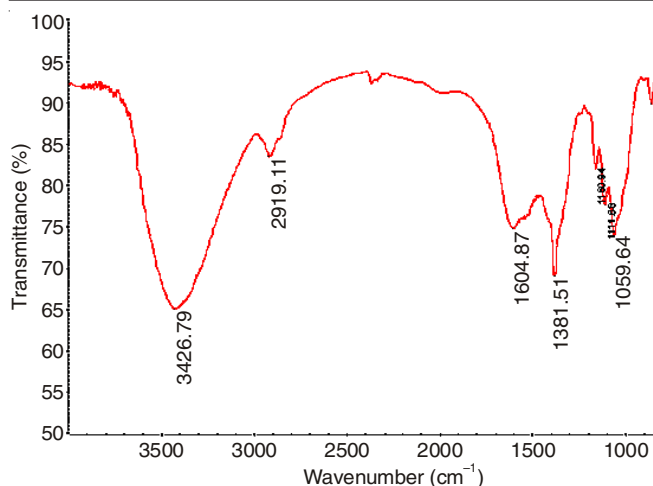


Fig. 1(b). FTIR spectrum of chitosan/sodium alginate bead

In addition to this a strong peak which was observed at 1638 cm^{-1} corresponding to the presence of $\text{C}=\text{N}$ stretching in the case of chitosan/sodium alginate bead prepared with glutaraldehyde as a crosslinking agent confirms that the glutaraldehyde gets cross linked effectively with the chitosan and sodium alginate. The FTIR spectrum of chitosan/sodium alginate bead formulation 2876 cm^{-1} corresponding to pure chitosan was shifted to 2919 cm^{-1} indicates the blend formation between sodium alginate and chitosan [16].

XRD studies: X-ray diffraction pattern of raw chitosan and chitosan/alginate bead was shown in the Fig. 2a and 2b. The XRD pattern of pure chitosan shows two peaks at the $2\theta = 10^\circ$ and 20° , the nature of the peak indicates the semi crystalline nature of chitosan. For the binary bead the XRD pattern shows the broad peak at $2\theta = 20, 23$ and 41° , which

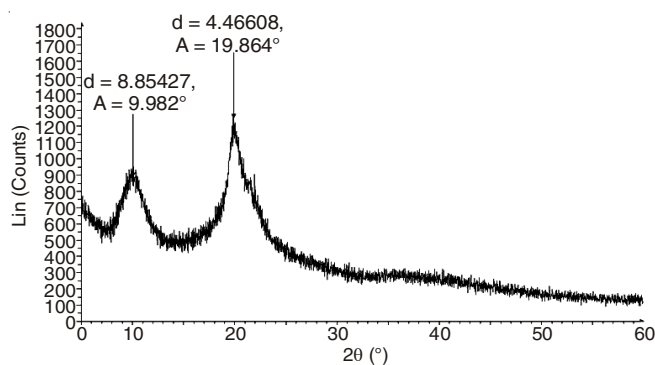


Fig. 2a. XRD pattern of chitosan

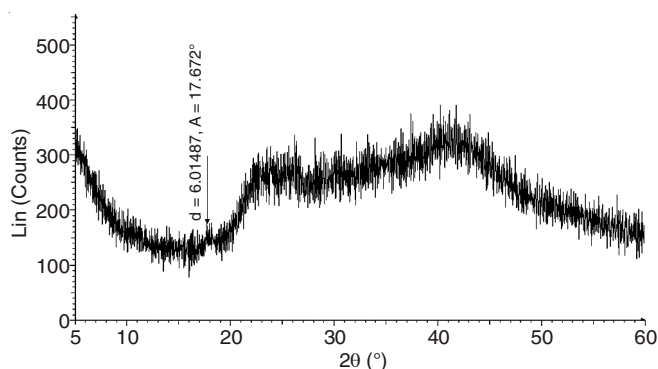


Fig. 2b. XRD diffractogram of chitosan/sodium alginate (1:1) bead

indicates the reduction of crystalline nature of the individual polymers during blending and bead formation. The observed shift in the peak and crystallinity confirms the effective blending and crosslinking. The increase amorphous nature of the prepared beads reveals the suitability of the material for wastewater treatment.

Batch adsorption studies

Effect of contact time: The effect of contact time on the adsorption of nickel and copper (Fig. 3) was investigated by keeping other parameters constant. From the results it can be concluded that both the metals *i.e.*, copper and nickel gets adsorbed more with the increase in the time of contact of the adsorbent with the metal. This happens because of the higher level of contact time of the copper and nickel ions with the adsorbent (chitosan/alginate). Due to limited mass transfer of the adsorbate molecules though the adsorption rate increases initially it attains equilibrium in due course of time.

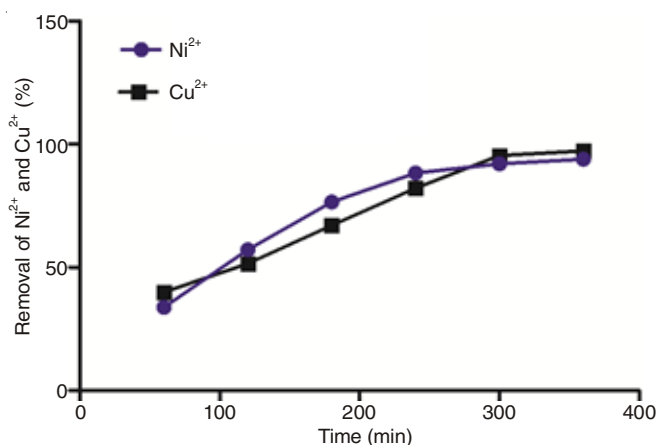


Fig. 3. Effect of contact time

Effect of pH: The adsorption capacity of the binary bead is strongly affected by the pH of the solution (Fig. 4). The removal efficiency of nickel and copper was investigated by varying the pH from 4 to 8. Initially the adsorption of copper and nickel were less at low pH like 4, 4.5 and 5. When the pH reached 5.5 the adsorption of nickel was the highest and then it decreased from pH 6-8. Similarly in case of copper, adsorption was increasing from 4 to 6 and reached maximum adsorption at pH 6 (91 %) and decreases with increase in pH from 6.5 to 8. This is because when the pH is low the number of protons available to protonate the functional group will be more that the functional sites will not be available for adsorption which reduces the metal ion adsorption. When pH increases, the number of protons decreases and therefore adsorption increases. The optimum pH for copper is 5.5 and 6 for nickel.

Effect of adsorbent dose: The effect of adsorbent dose on the metal ion removal was investigated by varying in the adsorbent dose from 1 to 6 g (Fig. 5). As the adsorbent dose increases, the adsorption also increases. As the dosage of adsorbent increases the available adsorbing sites will be more making more copper and nickel ions to get attached. The maximum percentage removal of copper is 89 % and nickel is 82 % at adsorbent dose of 6 g.

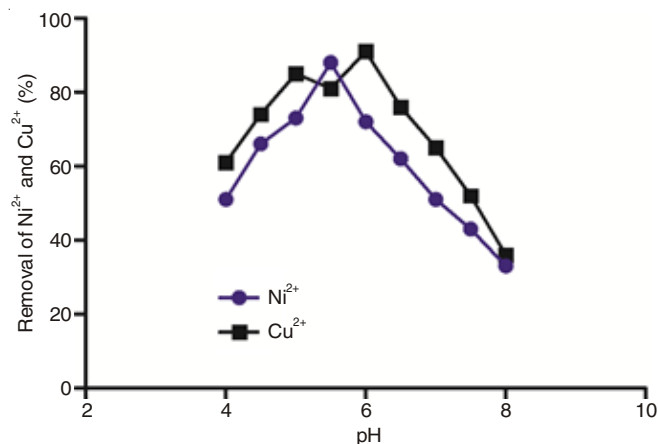


Fig. 4. Effect of pH

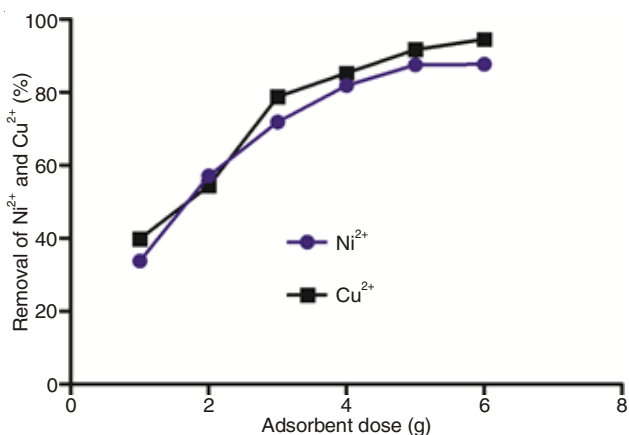


Fig. 5. Effect of adsorbent dose

Langmuir isotherm model: It is based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface. It is also assumed that there is same affinity for all the sites to adsorb monolayer of metal ions and there is no interaction between adsorbed molecules. The adsorption sites in chitosan/sodium alginate bead are identical in energy and as the intermolecular distance increases the force responsible for adsorption decreases.

Thus Langmuir isotherm is as depicted in the equation given below:

$$C_{ads} = (K_L C_{eq}) / (1 + b C_{eq})$$

Langmuir isotherm (linearized form) is given below:

$$C_{eq} / C_{ads} = b C_{eq} / K_L + 1 / K_L$$

$$C_{max} = K_L / b$$

where, C_{ads} is the amount of metal ion adsorbed (mg/g); C_{eq} is the concentration of metal ion in equilibrium in solution (mg/dm³); K_L represents Langmuir constant in dm³/g and B the Langmuir constant (dm³/mg); C_{max} is the maximum metal ion adsorbed.

A Langmuir adsorption isotherm plot of C_{eq} / C_{ads} vs. C_{eq} as shown in Fig. 6 shows almost a straight line which confirms the suitability of the Langmuir adsorption isotherm.

The Langmuir adsorption isotherm of copper and nickel ions was represented in Fig. 6a and 6b and Langmuir isotherm constant parameters are given in Table-1. The linearity of the two plots supports the monolayer adsorption and the biosorption depends on the concentration and pH of the metal solutions. For Langmuir isotherm model the homogeneous surface condition of adsorbent is required for monolayer adsorption. But the prepared crosslinked chitosan/alginate bead have heterogeneous surface for metal ion adsorption, therefore it may not follow the monolayer adsorption pattern. Hence the multilayer adsorption is expected in case of prepared crosslinked chitosan/sodium alginate bead.

Metal ion	Langmuir constants			
	K_L (dm ³ /g)	b (dm ³ /mg)	C_{max} (mg/g)	R^2
Ni(II)	0.5458	0.00333	163.90	0.5461
Cu(II)	0.7651	0.00496	154.25	0.5593

Freundlich isotherm model: This empirical model assumes heterogeneous surface exposed for adsorption of metal ion solutions which follow non ideal sorption as well as multilayer sorption. This is observed in heterogeneous surface energies in which the energy term (b) in the Langmuir equation varies as a function of surface coverage (q_e) strictly due to the variations in heat of adsorption. The widely used empirical Freundlich equation based on a heterogeneous surface was given by:

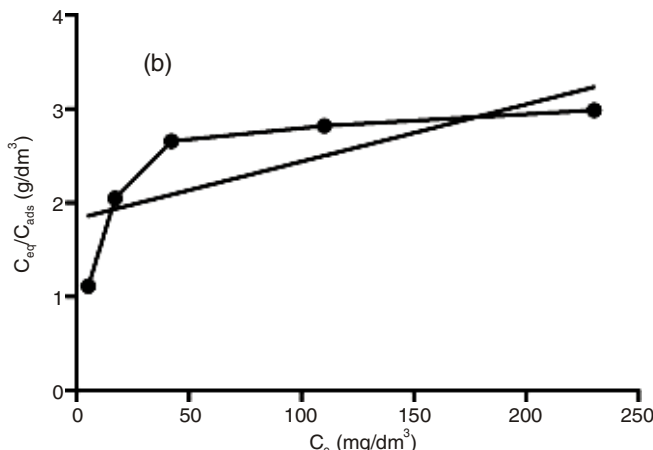
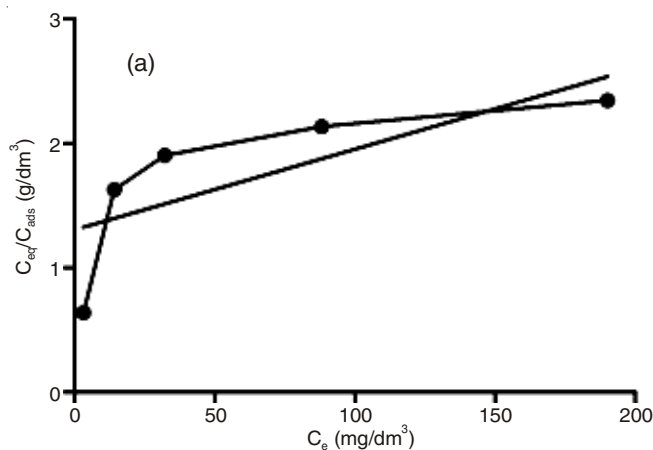


Fig. 6. Langmuir adsorption isotherm plot for (a) Ni(II) and (b) Cu(II) ions

$$q_e = K_f C_e^{1/n}$$

The linear form of Freundlich equation is expressed as:

$$\log q_e = \log K_f + 1/n \log C_e$$

A plot of $\log q_e$ versus $\log C_e$ gives a straight line of slope $(1/n)$ and an intercept of $\log K_f$.

For the experimental data $\log q_e$ is plotted against $\log C_e$ and is represented in Fig. 7 and Table-2. The correlation coefficients in the model fitting in Fig. 7 are found to be $R^2 = 0.9818$ and $R^2 = 0.9685$ respectively for copper and nickel ions. It is clear from the plot that Freundlich model fits well and describes the adsorptions of copper and nickel ions on the crosslinked chitosan/alginate beads much better than that of Langmuir model. It illustrates that the metal ions adsorption on chitosan-alginate beads was reasonably described by the Freundlich isotherm model. The Freundlich model is based on the principal of multilayer adsorption and also the adsorption on heterogeneous surfaces. The analysis hence confirms that the crosslinked chitosan/alginate beads were more heterogeneous

in the surface properties. The values of the Freundlich model constants K_f and n are found to be 1.1349 and 1.3319 for nickel ions and 1.7422 and 1.4275 for copper ions.

Pseudo first order kinetics: A linear form of pseudo-first order model was described by Lagergren (1898) in the form:

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$$

where q_e and q_t represent the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min); k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption process respectively. A plot which is linear of $\log (q_e - q_t)$ against time allows one to obtain the rate constant.

Pseudo second order kinetics: The pseudo-second-order rate equation can be represented as follows:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the adsorption rate constant of pseudo second order adsorption rate, respectively. A linear plot of (t/q_t) versus t drawn for the pseudo-second-order model was represented in Figs. 8 and 9.

The calculated correlation coefficients (Table-3) shows that it was close to unity for pseudo second order kinetics than first order kinetics for both Ni(II) and Cu(II) proving that the

Metal ion	Freundlich constants		R^2
	K_f (dm^3/g)	n (dm^3/mg)	
Ni(II)	1.1349	1.3319	0.9818
Cu(II)	1.7422	1.4275	0.9685

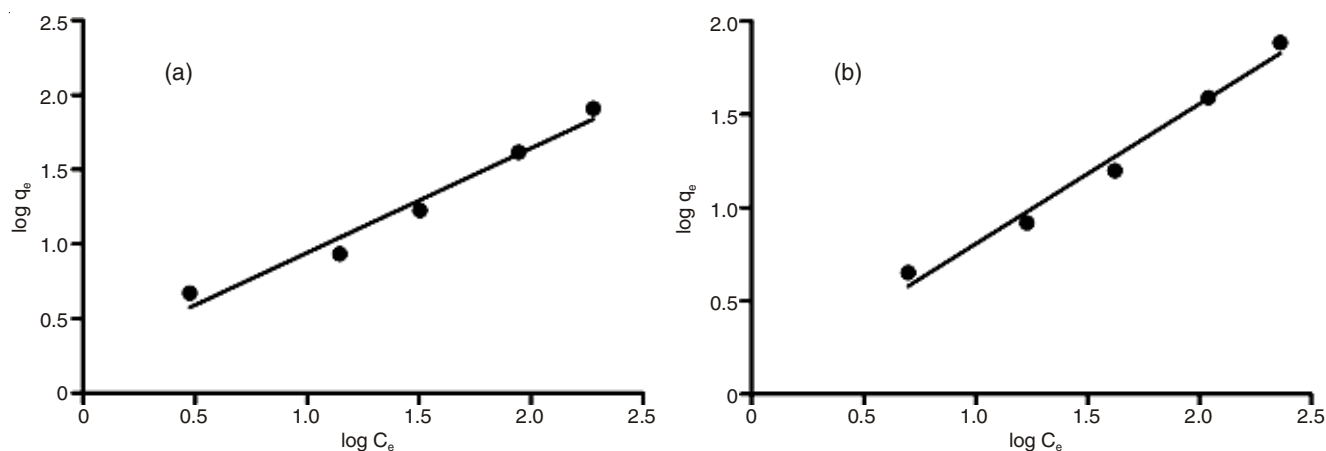


Fig. 7. Freundlich adsorption isotherm plot for (a) Ni(II) and (b) Cu(II) ions

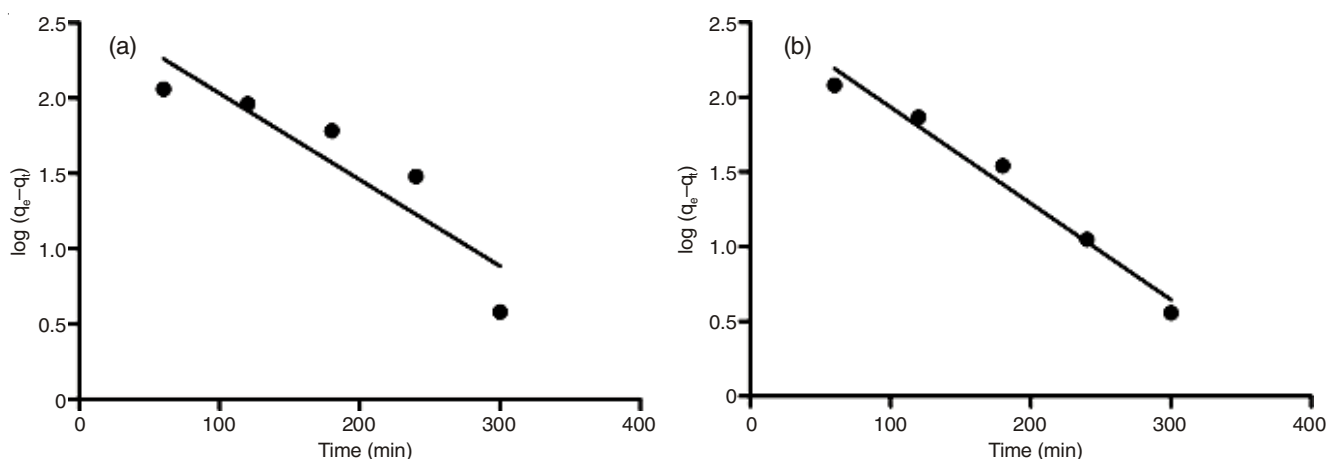


Fig. 8. Pseudo first order kinetic plot for (a) Ni(II) and (b) Cu(II) ions

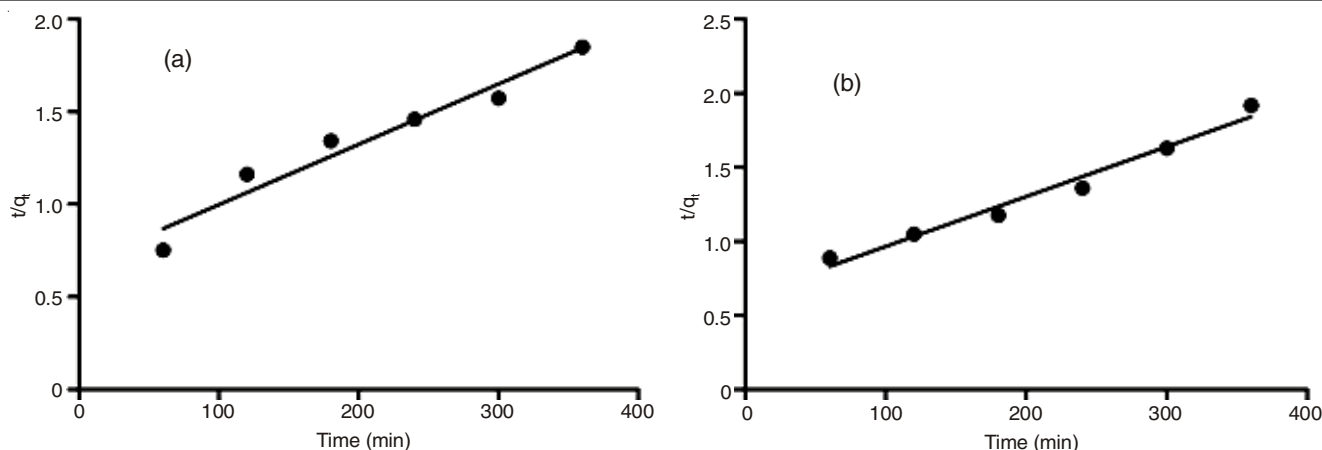


Fig. 9. Pseudo second order kinetic plot for (a) Ni(II) and (b) Cu(II) ions

TABLE-3
COMPARISON OF PSEUDO FIRST ORDER AND PSEUDO SECOND ORDER RATE CONSTANT

Metal ion	Pseudo-first-order kinetic model			Experimental value q_e (mg/g)	Pseudo-second-order kinetic model		
	q_e (mg/g)	k_1 (min^{-1})	R^2		q_e (mg/g)	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Ni(II)	400.37	0.006439	0.9742	180	186.99	0.003366	0.9843
Cu(II)	454.23	0.005735	0.8301	188	206.79	0.003255	0.9481

process adsorption follows the pseudo second order kinetics. In most of the cases, the first order equation is generally applicable over the initial stage of adsorption process and it does not fit well to the whole range of contact time [17]. The second order equation correlates well to the adsorption behaviour due to the participation of the adsorbent and adsorbate in the process of adsorption equally in the same manner and their concentration affects the mechanism significantly.

Conclusion

The present study deals with the successful synthesis and characterization of the chitosan/sodium alginate beads (1:1) in the presence of glutaraldehyde as a crosslinker. Efficient blending between chitosan/sodium alginate is proved from FT-IR spectral studies and the reduction in overall crystallinity of the prepared blend beads is evident from XRD studies. The addition of chitosan into sodium alginate made the beads materially denser and hence mechanically stronger. The chemical and thermal stability were improved by crosslinking the polymers with glutaraldehyde. Also the prepared chitosan/sodium alginate beads prepared in the presence of glutaraldehyde can be used as an effective adsorbent for nickel and copper ion removal from aqueous solutions and showed good adsorption capacities for both nickel and copper ions adsorption, although the adsorption performance was pH-dependent. Of the two isotherm models evaluated Freundlich isotherm model describe the adsorption isotherm of the crosslinked chitosan/alginate beads better than the Langmuir isotherm model. Metal ion on crosslinked chitosan/alginate beads is found to follow pseudo-

second-order kinetics. Thus the binary bead of chitosan, sodium alginate in the presence of glutaraldehyde crosslinker is very effective adsorbent for the removal of copper(II) and nickel(II). The adsorbent can be tested for other heavy metals also.

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