



Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads

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ABSTRACT

A new biosorbent was developed by coating chitosan, a naturally and abundantly available biopolymer, on to polyvinyl chloride (PVC) beads. The biosorbent was characterized by FTIR spectra, porosity and surface area analyses. Equilibrium and column flow adsorption characteristics of copper(II) and nickel(II) ions on the biosorbent were studied. The effect of pH, agitation time, concentration of adsorbate and amount of adsorbent on the extent of adsorption was investigated. The experimental data were fitted to Langmuir and Freundlich adsorption isotherms. The data were analyzed on the basis of Lagergren pseudo first order, pseudo-second order and Weber–Morris intraparticle diffusion models. The maximum monolayer adsorption capacity of chitosan coated PVC sorbent as obtained from Langmuir adsorption isotherm was found to be 87.9 mg g⁻¹ for Cu(II) and 120.5 mg g⁻¹ for Ni(II) ions, respectively. In addition, breakthrough curves were obtained from column flow experiments. The experimental results demonstrated that chitosan coated PVC beads could be used for the removal of Cu(II) and Ni(II) ions from aqueous medium through adsorption.

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1. Introduction

Techniques such as chemical precipitation, evaporation, electro deposition, ion exchange, adsorption, and membrane separation have been used to remove and recover metal ions from wastewater. However, these technologies are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations. Adsorption is highly effective, inexpensive and easy to operate among the physicochemical treatment processes. Consequently numerous low cost alternatives have been studied including fly ash (Rao et al., 2002), agricultural wastes (Marshall and Johns, 1996; Wafwoyo et al., 1999), banana pith (Low et al., 1995), chitin and chitosan (Sankaramakrishnan et al., 2006; Cheung et al., 2003; Jeon and Holl, 2004).

Chitosan is a partially deacetylated product of chitin, which has many useful features such as biocompatibility, biodegradability, and antibacterial property. The adsorption characteristics of Cu(II) and Ni(II) from aqueous solutions on chitosan and calcium alginate biopolymers, and their derivatives were investigated (Huang et al., 1996). Adsorption behavior of flake and bead types of chitosans prepared from fishery wastes towards metal and dye was compared (Wu et al., 2000). Several studies were conducted to improve

the properties of chitosan and to enhance its adsorption capacity and selectivity for trace metal ions. In order to overcome the difficulties associated with its softness and tendency to agglomerate or form a gel in aqueous solutions, modifications were carried out by coating chitosan on alumina for the removal of Cr(VI) (Veera et al., 2003), and on perlite for the removal of Cr(VI) (Sameem et al., 2003), and Cu(II) and Ni(II) (Kalyani et al., 2005).

The biosorbents prepared from shrimp chitin and crab chitosan were tested for their removal and recovery efficiency for Cd(II), Cr(III) and Ni(II) ions (Chui et al., 1996; Tseng et al., 1999). Ni and Xu (1996) synthesized a series of resins based on chitosan and investigated adsorption capacity, rate and selectivity for different metal ions. Wan Ngah et al. (2004) and Schmuhl et al. (2001) studied the removal of Cu(II) from aqueous solutions using chitosan, and chitosan cross-linked with glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether. Adsorption removal of Cu(II) ions from simulated rinse solutions containing several chelating agents was studied using chitosan (Juang et al., 1999). The effect of different organic acids on the capacity of chitosan flakes to remove heavy metal ions from aqueous solutions was reported by Bassi et al. (1999). Nickel imprinted chitosan resin (Tianwei et al., 2001) and cross-linked chitosan with copper as the template (Zuoying et al., 2001) were prepared to improve the adsorption capacity and selectivity for trace metal ions.

In this investigation an attempt was made to overcome the mass transfer limitations by synthesizing a biosorbent by coating chitosan on the surface of PVC beads. The biosorbent was

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characterized by FTIR spectral analysis, porosity and surface area measurements. The basic objectives of the study include; (1) to study the adsorption characteristics of Cu(II) and Ni(II) on chitosan coated PVC beads under equilibrium and column flow conditions, (2) to understand the kinetics and (3) to model the adsorption process. For this purpose, the effect of various factors affecting the adsorption process, such as time of contact, initial pH of the solution, adsorbent dose and metal ion concentration were investigated. The experimental data were fitted to Freundlich and Langmuir adsorption isotherm models. The results were also analyzed on the basis of Lagergren pseudo-first order, pseudo-second order kinetic equations and intraparticle diffusion model. Column adsorption studies were conducted to evaluate the metal adsorption capacity in a dynamic flow method and to obtain breakthrough curves.

2. Methods

2.1. Materials

Analytical grade nickel ammonium sulphate and copper sulphate were purchased from S.D. Fine Chemicals, for nickel(II) and copper(II) ion sources. Hydrochloric acid and sodium hydroxide used for pH adjustment were obtained from Chemical Drug House Ltd., India. Commercial PVC beads and chitosan were purchased from Aldrich Chemical Company, USA. Highly pure water is prepared in the laboratory by double distillation of deionised water in quartz distillation plant (Bhanu Scientific Company, Bangalore, India).

The stock solutions of Cu(II) and Ni(II) were prepared by dissolving 3.929 g of copper sulphate and 6.7302 g of nickel ammonium sulphate in 1000 mL of double distilled water such that each mL of the solution contains 1 mg of divalent metal. The exact concentration of each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1} . The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

2.2. Preparation of chitosan coated PVC beads

Medium molecular weight chitosan was sieved to remove dust and small particles. The sieved chitosan was boiled for 30 min and rinsed several times with deionized double distilled water to desorb any impurities from the chitosan. Then, dried under vacuum for 3 days and kept in desiccators before use. About 30 g of chitosan was slowly added to 1 L of 0.2 M oxalic acid solution under continuous stirring at 40–50 °C for about 4 h to facilitate the formation of viscous gel. The gel was allowed to stay over night to enable the gas bubbles to escape. PVC beads were first stirred with 0.2 M oxalic acid for 6 h at room temperature, filtered and washed with deionized water. About 60 g of acid treated PVC beads were slowly added to the diluted chitosan gel and stirred for 12 h at 40–50 °C. The beads coated with chitosan were then dropped into a 0.5 M NaOH precipitation bath to neutralize the excess acid. The beads were separated from NaOH bath, and washed several times with deionized distilled water to a neutral pH. The beads were dried in a freeze drier and stored in desiccators.

2.3. FTIR spectral and surface area analysis

Fourier transform Infrared spectra of biosorbent before and after adsorption of metal ions were recorded in the frequency range of 400–4000 cm^{-1} using FTIR spectrophotometer (Perkin-El-

mer-283B, USA). The samples were formed into pellets with KBr. Surface area of the chitosan coated PVC beads were measured by single point BET (Brunauer, Emmett and Teller) method using thermal conductivity detector (Carlo Erba Soptomatic – 1800) with in the range of 0.1–2000 $\text{m}^2 \text{g}^{-1}$ with the sample size of 2–10 mg. Pycnomatic ATC (automatic temperature control) is uniquely designed for density measurement of solid and powder samples. Porosity is defined as the fraction of apparent volume of the adsorbent that is attributed to the pores detected (Rouquerol et al., 1994). Pore volume, density and porosity of the biosorbent samples were measured using Pycnomatic ATC (Thermo Electronic Corporation, Italy). The cation exchange capacity (CEC) of the sorbent samples was obtained by the ammonium acetate solution procedure. In this method, 1.0 g biomass sample is dispersed in 20 mL of 1.00 M sodium acetate solution. The resulting suspension is mixed with 20 mL of 1.00 M ammonium acetate and mechanically stirred at room temperature for 1 h and centrifuged for 5 min to extract the Na^+ ions. The concentration of Na^+ ions in the extracted solution was determined by flame atomic absorption spectroscopy (FAAS), which represents CEC of sorbent. The surface charge density (SCD) was evaluated from the relation,

$$\text{SCD} = \text{CEC}/\text{SA} \quad (1)$$

where SA referred to the concentration of sodium acetate.

2.4. Equilibrium studies

Metal stock solutions were diluted to required concentrations for obtaining solutions containing 100–500 mg L^{-1} of Cu(II) or Ni(II) ions. Batch experimental studies were carried out with known weight of adsorbent and 100 mL of Cu(II) or Ni(II) solution of desired concentration at an optimum pH in 125 mL Erlenmeyer flasks. The flasks were agitated on a mechanical shaker (Ashok United Scientific Company, Chennai, India) at 120 rpm for a known period of time at room temperature. After attaining equilibrium, adsorbent was separated by filtration using Whatman filter paper and the aqueous-phase concentration of metal was determined with atomic absorption spectrophotometer (Perkin-Elmer 2380).

The equilibrium uptake capacity of the biosorbent for each metal ion was calculated according to mass balance,

$$q_e = \left(\frac{C_i - C_e}{m} \right) \cdot v \quad (2)$$

where q_e was the amount adsorbed per unit mass of adsorbent (mg g^{-1}), C_i and C_e were, respectively, initial and equilibrium concentrations of metal ion (mg L^{-1}), m was the mass of adsorbent (g) and v was volume of solution in liters. Control experiments were conducted with metal ion solutions in absence of biosorbent and found no metal adsorption by the walls of the container. Each experiment was repeated three times independently and the means were taken. Standard deviation and analytical errors were calculated and maximum error was found to be $\pm 5\%$. Error bars were included in the figures. The effect of pH of the medium on metal removal was studied by performing equilibrium sorption experiments at different pH values. A pH meter (Elico, Model, India) with combined glass electrode was used for pH measurements. Adjustment of pH was made with 0.1 N hydrochloric acid and 0.1 N sodium hydroxide solutions. The effect of pH was studied by keeping the metal ion concentration, the amount of biosorbent, contact time, and the temperature constant.

2.5. Column adsorption experiments

Column flow adsorption experiments were conducted in a glass column of about 2.5 cm internal diameter and 10 cm length. The column was packed with the adsorbent while shaking the column

so that maximum amount of adsorbent was packed without gaps. A constant flow rate (2 mL min^{-1}) was maintained throughout the experiment using peristaltic pump (Model 7518-10). The effluent solution was collected at different time intervals and the concentration of the metal ion in the effluent solution was monitored by atomic absorption spectrometry. The solutions were diluted appropriately prior to analysis. Break through curves for the adsorption of Cu(II) and Ni(II) on the biosorbent were obtained by plotting volume of the solution against the ratio of concentrations of metal ions in the effluent and in the influent solutions (C/C_0).

3. Results and discussion

3.1. Characterization of the biosorbent

The FTIR spectrum of chitosan coated PVC beads before adsorption indicates the presence of predominant peaks at 3351.7 cm^{-1} (–OH and –NH stretching), 2987.2 and 2901.4 cm^{-1} (–CH stretching), 1638.2 cm^{-1} (–NH bending in –NH₂), 1393.3 cm^{-1} (–NH deformation vibration in –NH₂), and 1065.5 cm^{-1} (–C–O–C– stretching). This reveals that all functional groups such as –NH₂, –OH, originally present in chitosan, are intact even after coating on PVC and are available for interaction with the metal ions. The peak at 672 cm^{-1} corresponds to stretching of C–Cl bond present in PVC. The FTIR spectra of sorbent after adsorption indicate a shift in absorption frequency of amino and hydroxyl groups. This may be attributed to the deformation of O–H and N–H bands as a result of interaction between the functional groups and metal ions.

The influence of the surface properties on the extent of adsorption was evaluated by measuring the surface area ($120.24 \text{ m}^2 \text{ g}^{-1}$), porosity (52.78%), pore volume ($0.167 \text{ cm}^3 \text{ g}^{-1}$), cation exchange capacity (CEC) (4.16 meq g^{-1}) and surface charge density (SCD) (0.034 meq m^{-2}). Porosity is one of the factors that influence the activity and physical interaction of solids with liquids and gases. The biosorbent developed has superior properties with 50% higher porosity. Similar improvement in the properties of chitosan/poly (vinyl alcohol) blend foams was reported by Wang et al. (2006). CEC indicates the improvement of the biomass surface towards the sorption of cationic species in solution. Further more, the surface charge density (SCD) gives an overall intensity of charges on the solid matrix surface. Transport studies conducted by Findon et al. (1993) suggested that copper is chelated with the NH₂ and OH groups in the chitosan chain. It was confirmed that the amino groups of chitosan are the major effective binding sites for metal ions, forming stable complexes by co-ordination (Chui et al., 1996). The electrons present on nitrogen in the amino groups can establish dative bonds with transitional metal ions. Some hydroxyl groups in these biopolymers may function as donors. Hence deprotonated hydroxyl groups involved in the co-ordination with metal ions (Lerivrey et al., 1986).

3.2. Effect of pH on biosorption of nickel(II) and copper(II) ions

The effect of pH on the adsorption of nickel(II) and copper(II) ions were studied at different pH values using chitosan coated PVC beads at constant metal ion concentration (100 mg L^{-1}) and amount of biosorbent (100 mg). The results indicate that the maximum uptake of Cu(II) ions takes place at pH 4.0 while the maximum uptake of Ni(II) ions occurs at an initial pH of 5.0. The adsorption capacity of the biosorbent increases with increase in pH of the medium. Similar trend was observed with the adsorption of copper from aqueous solution by chitosan (Chu, 2002). The low level of metal ion uptake by the biosorbent at lower pH values could be attributed to the increased concentration of hydrogen (H⁺) ions which compete along with Cu(II) and Ni(II) ions for binding sites on the biomass. As the pH is lowered, the overall surface

charge on the beads become positive, which will inhibit the approach of positively charged metal cations. At pH values above the isoelectric point, there is a net negative charge on the surface and the ionic point of ligands such as carboxyl, hydroxyl and amino groups are free so as to promote interaction with the metal cations (Quek et al. 1998). This would lead to electrostatic attractions between positively charged cations such as Cu(II) and Ni(II) and negatively charged binding sites.

3.3. Effect of agitation time and kinetics of metal sorption

The effect of agitation time on the extent of adsorption of metals at different concentrations is shown in Figs. 1 and 2 for Cu(II) and Ni(II), respectively. The extent of adsorption increases with time and attained equilibrium for all the concentrations of copper and nickel studied (100, 250 and 500 mg/L) at 210 and 240 min, respectively. After this equilibrium period, the amount of metal adsorbed did not change significantly with time. The amount of metal adsorbed versus time curves are smooth and continuous.

In order to investigate the mechanism of sorption, the rate constants of sorption process were determined by using Lagergren first order and a pseudo-second order kinetic models. The values of the first and second order rate constants are included in Table 1. In many cases the first order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (McKay and Ho, 1999). The second order kinetic model assumes that the rate limiting step may be chemical adsorption (Chiou and Li, 2002). In many cases, the adsorption data could be well correlated by second order rate equation over the entire period of contact time (Sag and Aytay, 2002). The results of the present study indicate that the adsorption of Cu(II) and Ni(II) on chitosan coated PVC beads follows second order kinetic model.

The results were also analyzed in terms intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate controlling step in adsorption of Cu(II) and Ni(II) on chitosan coated PVC beads. The model proposed by Weber and Morris (1963) can be written as, $q_t = K_{id}t^{1/2}$, where K_{id} ($\text{mg g}^{-1} \text{ min}^{-1/2}$) is the rate constant of intraparticle diffusion. The Weber–Morris plots for adsorption of Ni(II) and Cu(II) are given in Fig. 3. If the intraparticle diffusion is the sole rate determining step, the plots of q_t vs. $t^{1/2}$ should be linear and pass through the origin (Ozcan and Ozcan, 2005). The plots in the figure are multi linear with three distinct regions indicating three different kinetic mechanisms. The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intraparticle

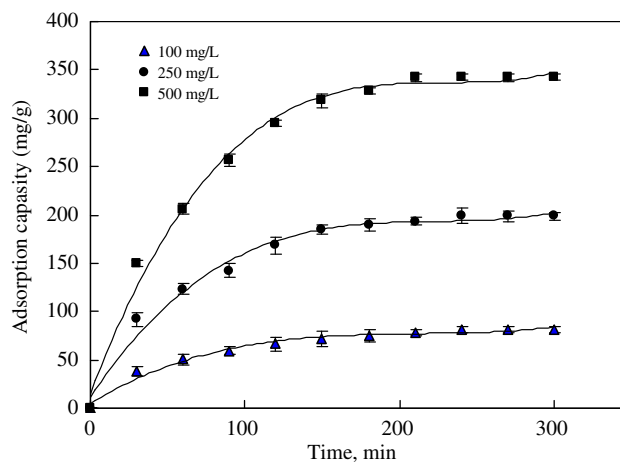


Fig. 1. Effect of time on biosorption of copper(II) on chitosan coated PVC beads.

diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on the results it may be concluded that intra particle diffusion is not only the rate determining factor.

3.4. Effect of adsorbent dose

One of the parameters that strongly affect the biosorption capacity is the amount of the biosorbent. The dependence of Cu(II) and Ni(II) sorption on chitosan coated PVC was studied by varying the amount of the adsorbent from 0.05 g to 0.5 g while keeping the other parameters such as pH, metal solution volume (100 mL), concentration (100 mg/L), and contact time (240 min) constant. In both cases the removal percentage increases with increasing adsorbent dose (Fig. 4) from 64% to 94% and 68% to 96% in case of Cu(II) and Ni(II), respectively. However, the uptake capacity of metal ion per unit mass of biosorbent (mg g^{-1}) decreases with increase in dose of adsorbent, which may be due to lower utilization of adsorption capacity of the sorbent at higher dosage.

3.5. Equilibrium modeling

Analysis of the equilibrium data is important to develop an equation which accurately represents the adsorption process and which could be used for design purposes. Langmuir and Freundlich adsorption isotherms were used to fit the experimental data. To obtain the isotherms, initial concentration of Cu(II) and Ni(II) were varied from 100 to 500 mg/L while keeping the weight of chitosan coated PVC beads, pH and contact time constant. The Langmuir isotherm assumes monolayer adsorption whereas the Freundlich isotherm is an empirical model that is based on sorption on heterogeneous surface. The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots, are presented in Table 2 along with the correlation coefficient. Both the models are capable of representing the data adequately. The magnitude of the Freundlich constants, K_F and n indicate that the

uptake of Cu(II) and Ni(II) from aqueous solutions by the chitosan coated PVC is feasible. Langmuir constant, Q^0 , represents the maximum monolayer adsorption capacity of the biosorbent. The values are 87.9 mg g^{-1} and 120.5 mg g^{-1} for Cu(II) and Ni(II), respectively. Adsorption capacities of chitosan and modified chitosan sorbents, collected from the literature, are included in Table 3 along with the values corresponding to chitosan coated PVC for comparison. The sorbent developed in the present study exhibits higher adsorp-

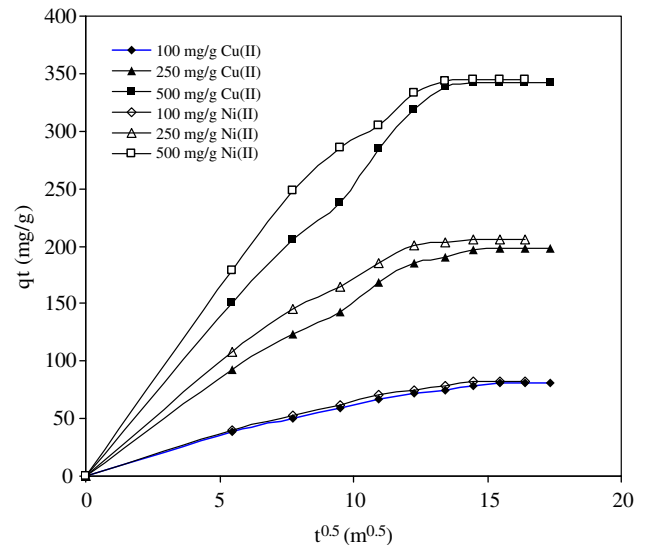


Fig. 3. Weber-Morris plots for adsorption of Cu(II) and Ni(II) on chitosan coated PVC beads.

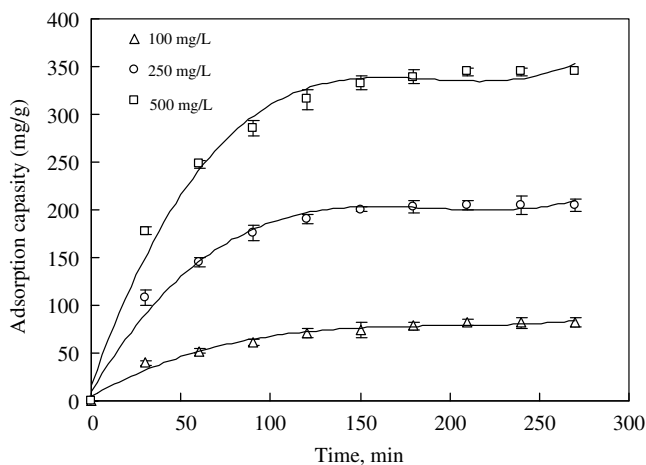


Fig. 2. Effect of time on biosorption of nickel(II) on chitosan coated PVC beads.

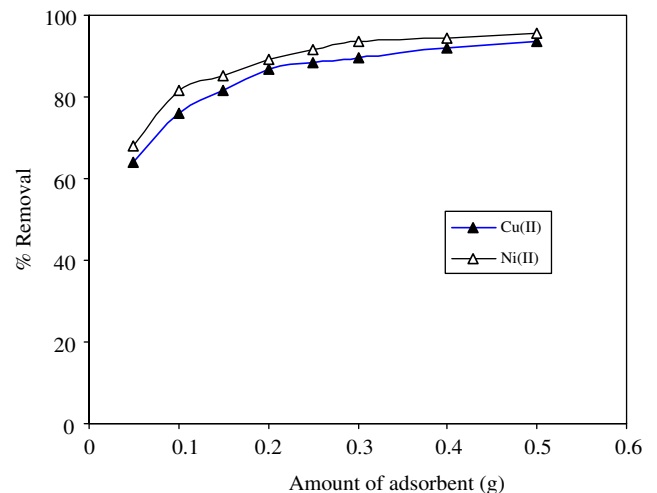


Fig. 4. Effect of amount of chitosan coated PVC beads on percent removal of copper(II) and nickel(II) ions.

Table 1

First order (k_1) and second order (k_2) rate constants for adsorption of Cu(II) and Ni(II) on chitosan coated PVC

Concentration of metal ion (mg L^{-1})	Cu(II)				Ni(II)			
	k_1	R^2	k_2	R^2	k_1	R^2	k_2	R^2
100	0.015	0.961	1.98×10^{-4}	0.998	0.017	0.980	2.12×10^{-4}	0.997
250	0.021	0.940	0.84×10^{-4}	0.995	0.026	0.952	1.21×10^{-4}	0.997
500	0.024	0.870	0.43×10^{-4}	0.991	0.029	0.879	0.73×10^{-4}	0.998

Table 2

Langmuir and Freundlich constants for the adsorption of Cu(II) and Ni(II) on chitosan coated PVC beads

Metal ion	Langmuir constants			Freundlich constants		
	Q^o (mg g ⁻¹)	b (L ⁻¹ mg)	R^2	K_f	N	R^2
Cu(II)	87.92	0.011	0.9866	0.1395	0.547	0.9828
Ni(II)	120.5	0.035	0.9932	0.0156	0.324	0.9687

Table 3Maximum adsorption capacity (mg g⁻¹) of different chitosan based adsorbents for Cu(II) and Ni(II)

Adsorbent	Maximum adsorption capacity (mg g ⁻¹)		pH	References
	Cu(II)	Ni(II)		
Chitosan	71.2		4.5	Cheung et al. (2003)
Chitosan	16.8	2.4	5.0	Huang et al. (1996)
Chitosan coated perlite	196.1	114.9	5.0	Kalyani et al. (2005)
Chitosan	59.0		5.0	Findon et al. (1993)
EDTA–Chitosan		123.3	2.0	Inoue et al. (1999)
DTPA–Chitosan		117.4	2.0	Mcafee et al. (2001)
Chitosan	33.4		6.0	Wan Ngah et al. (2004)
Chitosan/PVA	47.9		6.0	Wan Ngah et al. (2004)
Non-cross linked chitosan	80		5.0	Schmuhl et al. (2001)
Chitosan acetate crown ether (CCTS-1)	23.9	0.7	5.6	Tan et al. (1999)
Chitosan diacetate crown ether (CCTS-2)	31.3	4.1	5.6	Tan et al., (1999)
Epichlorohydrine cross-linked chitosan (CCTS)	16.8	6.4	5.6	Tan et al., (1999)
Chitosan coated PVC	87.9	120.5	4.0–5.0 ^a	Present study

^a For Cu(II) pH 4.0, Ni(II) pH 5.0.

tion capacity compared to chitosan in its natural form and most of the modified forms.

3.6. Column studies

The way in which an experiment is carried out is another parameter that can affect the capacity of a particular type of adsorbent to sequester metals. Since in batch experiments the concentration of adsorbate and the solution pH vary with time, the same parameters undergo a change along with the length of the column in continuous flow experiments. The flow rate in packed column is 2 mL m⁻¹ and the residence time of metal ions through the column is 5.3 min. The concentration profiles of the solution coming out of the column show that metal removal is fast and highly effective during the initial phase. Subsequently metal removal decreases, as a consequence of the progressive saturation of the binding sites. After passing about 300 mL of solution of metal ion solution through the column, the column gets saturated. The adsorption capacity of the biomass in each column is obtained by dividing the concentration of metal adsorbed by the total amount of biomass used. From these studies it can be concluded that chitosan coated PVC beads is a good biosorbent for removal of copper and nickel from aqueous medium.

4. Conclusions

In this study, chitosan coated PVC beads were developed and used as a biosorbent for the removal of copper(II) and nickel(II) ions from aqueous solution. The biosorbent is characterized on the basis of FTIR spectral study and analysis of surface morphology. The Langmuir adsorption model and Freundlich equation are used for the mathematical description of the biosorption of Cu(II) and Ni(II) ions onto chitosan coated PVC beads. The maximum adsorption capacities of chitosan coated PVC beads used in this study are 87.9 mg g⁻¹ for copper and 120.5 mg g⁻¹ for nickel. Batch equilibrium results suggest that the adsorption process follows second order kinetic model in both the cases. Column experiments show that it is possible to remove the metal ions from aqueous medium through biosorption on to chitosan coated PVC beads.

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