# Competitive adsorption of Cu (II), Co (II) and Ni (II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent

Kalyani Swayampakula[a], Veera M. Boddu[b], Siva Kumar Nadavala[a], Krishnaiah Abburi[a],*

[a] Biopolymers and Thermophysical Laboratories, Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India
[b] US Army Engineering Research and Development Center (ERDC), Construction Engineering Research Laboratories, Environmental Process Branch (CN-E), Champaign, IL 61826, United States

## ABSTRACT

A new composite chitosan-coated biosorbent was prepared and was used for the removal and recovery of heavy metals from aqueous solution. In the present investigation, equilibrium adsorption characteristics of Cu (II), Ni (II), and Co (II) from their binary and tertiary solution on newly developed biosorbent chitosan-coated perlite beads were evaluated through batch and column studies. These beads were characterized by using FTIR, EDXRF and surface area analysis techniques. The effect of various biosorption parameters like effect of pH, agitation time, concentration of adsorbate and amount of adsorbent on extent of adsorption was investigated. The adsorption follows Lagergren first order kinetic model. The equilibrium adsorption data were fitted to Freundlich and Langmuir adsorption isotherm models and the model parameters were evaluated. Both the models represent the experimental data satisfactorily. The sorbent loaded with metal was regenerated with 0.1N NaOH solution. Furthermore the column dynamic studies indicate the re-usage of the biosorbent.

© 2009 Published by Elsevier B.V.

## 1. Introduction

Concentrations of many trace metals in the aquatic environment have been reduced over the last few decades, through the implementation of Environmental Quality Standards. Owing to their adverse effects on human beings, a number of techniques such as filtration, reverse osmosis, chemical precipitation, ion exchange, electro-deposition and adsorption have been used to remove the toxic metals from aquatic environment [1]. However, these technologies are most suitable in situations where the concentrations of heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations [2]. Adsorption is an alternative technology and is highly effective, cheap and easy method among the physicochemical treatment processes. Adsorption on activated carbon has been found to be an effective process for metal removal, but it is too expensive. Consequently numerous low cost alternatives have been studied including activated carbon [3], activated slag [4] iron oxide coated sand [5], bagasse fly ash [6–9], natural zeolites [10], agricultural wastes [11], red mud [12,13], phosphatic clay [14], brewery's waste biomass [15], microbial and plant derived biomass [16], living and non-living algal biomass [17–22] chitin and chitosan [23,24].

Chitosan is a polycationic polymer derived from chitin, a major component of arthropods, and is readily available from sea food processing wastes [25]. Because chitosan has unique physiological and biological properties, it has been widely used as a versatile starting material for the preparation of various products in biomedical engineering [26]. In recent years, chitosan has also increasingly been studied as an adsorbent for the removal of heavy metal ions from aqueous solutions because the amino and hydroxyl groups on the chitosan chain act as a chelation or reaction sites for the substances to be removed [27,28]. Several investigators have attempted to modify chitosan to facilitate mass transfer and to expose the active binding sites to enhance the adsorption capacity. Grafting specific functional groups onto native chitosan backbone allows its sorption properties to be enhanced [29]. To overcome some of the problems associated with the use of pure chitosan, it is chemically modified by cross-linking or coating and is used as adsorbent [30,31].

In this study a new composite chitosan biosorbent is prepared by coating chitosan, a glucosamine biopolymer, over perlite, an inorganic porous aluminosilicate and formed into beads. Perlite is a siliceous volcanic glassy rock with an amorphous structure. It is expected that the more active sites of chitosan will be available due to the coating thus enhancing the adsorption capacity. The percent of chitosan-coated on perlite is determined by pyrolysis technique. Surface area, pore volume and pore diameter are obtained on the basis of Brunauer, Emmett and Teller (BET) and pycnomatic ATC. The chitosan-coated perlite (CCP) beads are characterized before

and after adsorption of metal ions by Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray fluorescence spectrometry (EDXRF). In the present investigation, equilibrium and dynamic column adsorption characteristics of Cu (II), Co (II) and Ni (II) metal ions from their binary and tertiary solute solutions, on newly developed biosorbent chitosan-coated perlite beads, are studied.

## 2. Materials and methods

### 2.1. Materials

The expanded form of perlite was obtained from Silbrico Corporations, IL, USA, and was used as a substrate for the preparation of beads. Chitosan (molecular weight 1–3 lakhs), analytical grade anhydrous, powdered copper (II) sulfate (≥99.99% trace metals basis), ammonium nickel (II) sulfate hexahydrate (≥99.99% trace metals basis) and cobalt (II) sulfate heptahydrate (≥99%) were procured from Aldrich Chemical Corporation. 99% pure oxalic acid dihydrate and NaOH beads (95–100%) and HCl (35% content, extra pure grade) were purchased from Fisher Scientific Company. Metal-bearing stock solutions were prepared (1000 ppm of Cu (II), Ni (II) and Co (II)) by dissolving the $CuSO_4$, $(NH_4)_2$ Ni $(SO_4)_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ metal salts (analytical grade) in double distilled water. The pH 5 of the experimental solutions was adjusted by adding 0.1N NaOH or 0.1N HCl solutions. All the working solutions were obtained by diluting the stock solution with double distilled water.

### 2.2. Synthesis of chitosan-coated perlite (CCP) biosorbent

The highly porous nature of chitosan-coated perlite (CCP) beads was prepared by drop wise addition of CCP gel into a 0.70 mg g$^{-1}$ NaOH precipitation bath was described in the earlier literature [32]. The purpose of adding acidic perlite–chitosan mixture to NaOH solution is to assist rapid neutralization of oxalic acid, so that the spherical shape could be retained. The beads are separated from NaOH bath, and washed several times with deionized water to a neutral pH. The beads are dried in a freeze drier, oven and by air. The biosorbent was characterized by pyrolysis, Fourier transform infrared spectroscopy, X-ray fluorescence studies and surface area analysis.

### 2.3. Biosorbent characterization

#### 2.3.1. Fourier transform infrared (FTIR) studies

FTIR spectra of chitosan-coated perlite (CCP) beads before and after adsorption of metal ions are recorded in the frequency range of 400–4000 cm$^{-1}$ on a Bomen FTIR, MB-series using a Nicolet–740, Perkin–Elmer–283B Fourier transform infrared spectrophotometer.

#### 2.3.2. Energy dispersive X-ray fluorescence (EDXRF) studies

EDXRF is used for the qualitative analysis of metal ions adsorbed on CCP beads using PAN analytical instrument (Netherlands) of energy dispersive X-ray fluorescence spectrophotometer. For this analysis the CCP beads are ground into fine powder and mixed with a binder (cellulose powder) and pressed into a thin pellet of 2.5 cm in diameter. The pellet is used for irradiation. The set-up calibrated using standard radioactive source and the geometry is kept constant for all the subsequent measurements.

#### 2.3.3. Brunauer, Emmett and Teller (BET) studies

Surface area of the CCP beads is measured by using Micrometrics (USA) BET (Brunauer, Emmett and Teller) instrument using nitrogen intrusion technique. The microstructure of the sorbent was characterized using physical adsorption/desorption of nitrogen at −196 °C. The samples are analyzed with an elemental analyzer, and on the basis of difference in the nitrogen content. Nitrogen isotherms are measured with an ASAP 2000 micro pore analyzer at 77 K.

#### 2.3.4. Scanning electron microscope (SEM) studies

Scanning electron micrographs are taken for the CCP beads, using a soft ware controlled digital scanning electron microscope-JEOLJSM 5410, Japan (Eucentric Gonimeter State type). In this microscope, very fine pencils of electrons are used for illumination, which scans the surface of the beads, much as a screen is scanned in a television tube. The wavelength of the electron beam is very short (0.05–0.005 Å), which are produced by a filament heated by high voltage.

### 2.4. Experimental procedure

#### 2.4.1. Batch studies

Batch sorption experiments were performed under agitation on mechanical shaker at 200 rpm by the addition of a measured quantity of CCP bead to 100 ml of metal solution in a 250 ml Erlenmeyer flask for a known period of time at room temperature (25.0 ± 0.5 °C). The equilibrium solution was separated from the biomass by vacuum filtration through membrane filters (0.5 μm) and the metal ion concentrations of the solutions at time 0 and at equilibrium was determined by atomic absorption spectroscopy. Metal uptake $Q'_e$ (mg g$^{-1}$) was calculated from the difference in the metal contents in the aqueous solution (mg L$^{-1}$), before and after adsorption and to the dry weight (g L$^{-1}$) of the CCP beads. The pH of the solutions was adjusted by adding 0.1N NaOH or 0.1N HCl solutions. The pH was measured using a Beckman $\Phi$32 pH meter (Beckman Instruments, Fullerton, CA). Adsorption of metal on the glassware was found to be negligible and was determined by running blank experiments. Experimental values of metal uptake capacities were the results of triplicate experiments reported as means. The amount adsorbed per unit mass of adsorbent at equilibrium $Q_e$ (mg g$^{-1}$) was obtained using the equation.

$$Q_e = \left( \frac{C_o - C_e}{m} \right) v \tag{1}$$

where $C_o$ and $C_e$ denote the initial and equilibrium metal ion concentrations (ppm), respectively. '$v$' was the volume of the solution in liters and '$m$' was the mass of the adsorbent used (g).

#### 2.4.2. Column adsorption studies

Dynamic flow adsorption studies were carried out in a pyrex glass column of about 1.35 cm internal diameter and 1.5 cm length. The column was filled with 1 g of the chitosan-coated on perlite beads by tapping so that the column was filled without gaps. The column was fully jacketed to circulate water from a constant temperature water bath, enabling the experiment to be carried out at a constant temperature. The adsorbent was washed thoroughly with water and dried prior to use. The column was packed with the dried adsorbent and shaken so that the maximum amount of adsorbent was packed in the column without gaps. Then it was fixed to a stand to keep it exactly perpendicular. The influent solution containing known concentration of aqueous metal solution was allowed to pass through the bed at constant flow rate was maintained throughout the run, 1 ml min$^{-1}$, in down flow manner. The pH of the solution was adjusted to 5.0 by adding 0.1N NaOH or 0.1N HCl solutions. The complete cycles of operation of each column experiment include three steps: pH pre condition, tracer injection, and metal adsorption until column exhaustion occurred. The effluent solution was collected time intervals, and the concentration of the metal ion in the effluent solution was monitored by Perkin – Elimer 2380 model Atomic absorption spectrophotometer. The solutions were diluted appropriately prior to analysis. All experiments were carried out in room temperature at 25.0 ± 0.5 °C.

### 2.4.3. Desorption studies

Desorption (recovery) studies were very important since the success of adsorption process depends on the regeneration of adsorbent. After the column was exhausted, the remaining aqueous solution in the column was drained off by pumping air. Desorption of solutes from loaded adsorbent was carried out by solvent elution method using 0.1 N NaOH as an eluent maintained at constant temperature at a fixed flow rate (1 ml min$^{-1}$). The effluent samples at different intervals like 5 min, 10 min, 20 min, 30 min and so on, were collected at the bottom of the column for analysis. After the regeneration, the adsorbent column was washed with distilled water to remove NaOH from the column before the influent metal solution was reintroduced for the subsequent adsorption–desorption cycles. Adsorption–desorption cycles were performed thrice for each solution mixture using the same bed to check the sustainability of the bed for repeated use.

## 3. Results and discussion

### 3.1. Pyrolysis studies

The amount of chitosan-coated on perlite was obtained by measuring the weight loss of biosorbent from pyrolysis. Pyroly-sis experiments were conducted at high temperatures (800 °C) to determine the amount of chitosan-coated over perlite. Two ceramic crucibles one containing acid washed pure perlite and the other containing chitosan-coated perlite (CCP) beads were placed inside a furnace heated to 800 °C. The chitosan burnt out at this temperature and the chitosan content was determined from weight difference. The results indicated that 23% of chitosan was coated over perlite.

### 3.2. Surface area analysis

Surface area, density, pore volume, pore diameter and porosity of the composite biosorbent were determined with BET (Brunauer, Emmett and Teller) instrument (Model No: Micromeritirics, USA). The isotherm plots were used to calculate the specific surface area (N$_2$/BET method) and average pore diameter of CCP, while micropore volume was calculated from the volume of nitrogen adsorbed at $p/p_o$ 1.4. The sorbent material shows an average surface area of 112.25 m$^2$ g$^{-1}$ and pore volume of 0.47 cm$^3$ g$^{-1}$, porosity of 43.41%, pore diameter of 0.97 nm and density of 3.13 g cm$^{-3}$.

### 3.3. Fourier transform infrared (FTIR) studies

FTIR spectra of CCP in virgin form and loaded with metal ion, obtained using a Nicolet–740, Perkin–Elmer model 283B spectrophotometer (USA) are shown in Fig. 1a–e. The FTIR spectrum of CCP in Fig. 1a indicates the presence of predominant peaks at 3360 cm$^{-1}$ (–OH and –NH stretching vibrations), 2978 and 2900 cm$^{-1}$ (–CH stretching vibration in –CH and –CH$_2$), 1641 cm$^{-1}$ (–NH bending vibration in –NH$_2$), 1395 cm$^{-1}$ (–NH
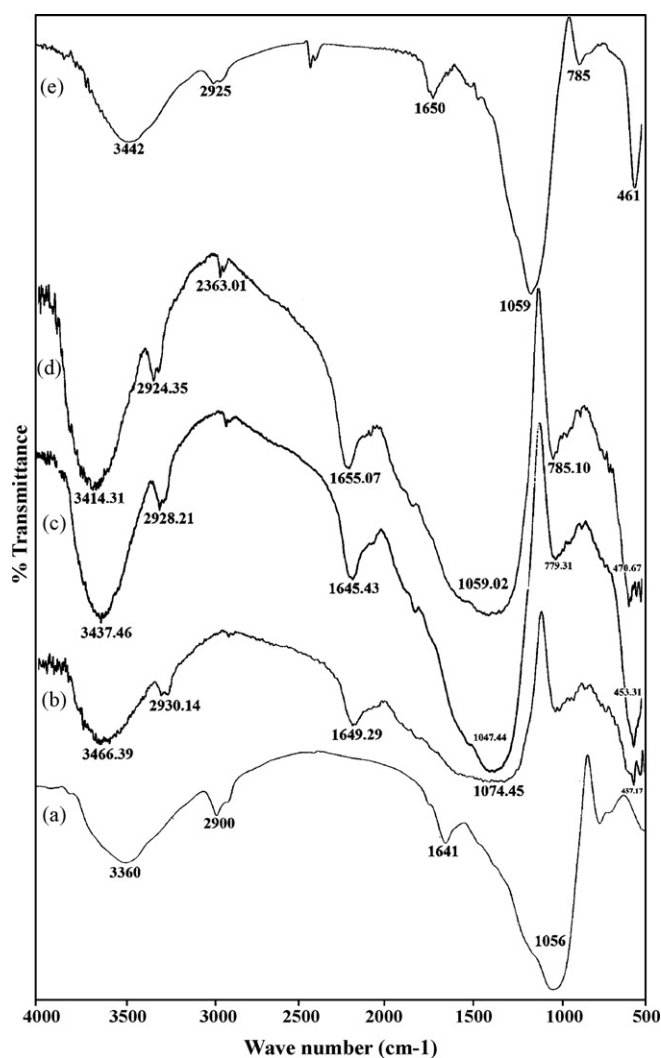


**Fig. 1.** FTIR spectrum of: (a) chitosan-coated perlite beads, (b) after adsorption of Cu (II) and Ni (II) ions, (c) after adsorption of Cu (II) and Co (II) ions, (d) after adsorption of Ni (II) and Co (II) ions and (e) after adsorption of Cu (II), Co (II) and Ni (II) ions.
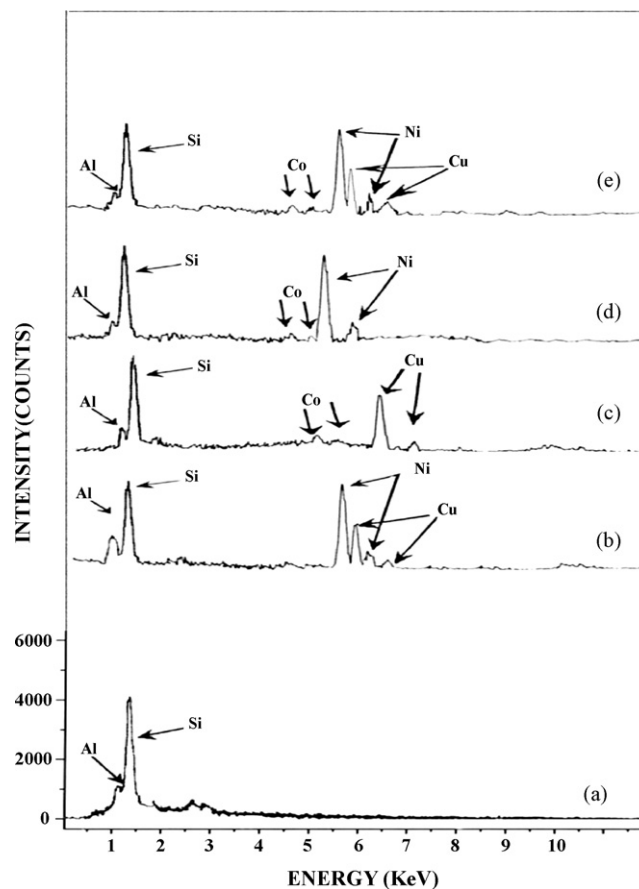


**Fig. 2.** EDXRF spectrum of: (a) unexposed chitosan-coated perlite, (b) after adsorption of Cu (II) and Ni (II), (c) after adsorption of Cu (II) and Co (II), (d) after adsorption of Co (II) and Ni (II) and (e) after adsorption of Cu (II), Co (II) and Ni (II).

deformation vibration in –NH$_2$), and 1056 cm$^{-1}$ (–CO stretching vibration in -COH). The peaks at these wave numbers were intact, indicating that the functional groups were not disturbed during the coating process and are available for interaction with the metal ions. The intensity of transmittance of peaks were relatively more in case of metal ions (viz., Cu (II), Co (II) and Ni (II))—loaded CCP (Fig. 1b–e,) compared with unloaded CCP. This may be attributed due to the interaction between the functional groups and metal ions during the adsorption process. This observation is evidence that functional groups such as –NH$_2$, –OH, and –CO– are involved in binding the metal ions to CCP.

Based on the transport studies copper was chelated with the NH$_2$ and OH groups in chitosan matrix [33] and was confirmed that the amino groups of chitosan were the major effective binding sites for metal ions, forming stable complexes by co-ordination [34]. 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 were supposed to be involved in the co-ordination with metal ions [35] and chitosan forms chelate with metal ions by releasing hydrogen ions [36].

### 3.4. Energy dispersive X-ray fluorescence (EDXRF) spectroscopic studies

EDXRF spectra of CCP beads before and after their exposure to metal solutions, obtained on PAN analytical instrument (Netherlands), are shown in Fig. 2a–e. The EDXRF spectrum of unexposed CCP beads was presented in Fig. 2a indicates the peaks assigned to aluminum and silicon, which were the two major, constituents of perlite. The EDXRF spectra of CCP treated with aqueous metal solutions of Cu (II), Co (II) and Ni (II) from their binary and tertiary solutions were shown in Fig. 2b–e. The presence of peaks of different metal ions was observed in these figures, which provides an evidence for metal uptake by chitosan. Strong peaks of $K_\alpha$ and $K_\beta$ values at 8.04 and 8.94 keV, respectively were due to uptake of Cu (II), peaks at 6.92 and 7.69 keV were due to adsorption of Co (II) and peaks at 7.46 and 8.30 keV indicate the presence of Ni (II). It was an evident that highly porous chitosan beads were capable of adsorbing metal ions from their aqueous solution.

### 3.5. Scanning electron microscopic (SEM) studies

The SEM of various samples given in Fig. 3a–f is taken to study the surface morphology. The SEM micrograph of the outer surface of CCP beads is shown in Fig. 3a. The average size of particles is 100–150 μm and that the shape of composite particle can be described as spherical. The figure also illustrates the surface texture and porosity of CCP beads with holes and small openings on the surface, thereby increasing the contact area, which facilitates the pore diffusion during adsorption. The beads are cut into half and then the SEM of the internal surface is recorded and included in Fig. 3b. The porous nature is clearly evident from this micrograph. The inner surface appears to have similar type of texture and morphology as the outer surface. Fig. 3c–f describes the surface characteristics and morphology of the beads after their exposure to metal ion solutions.
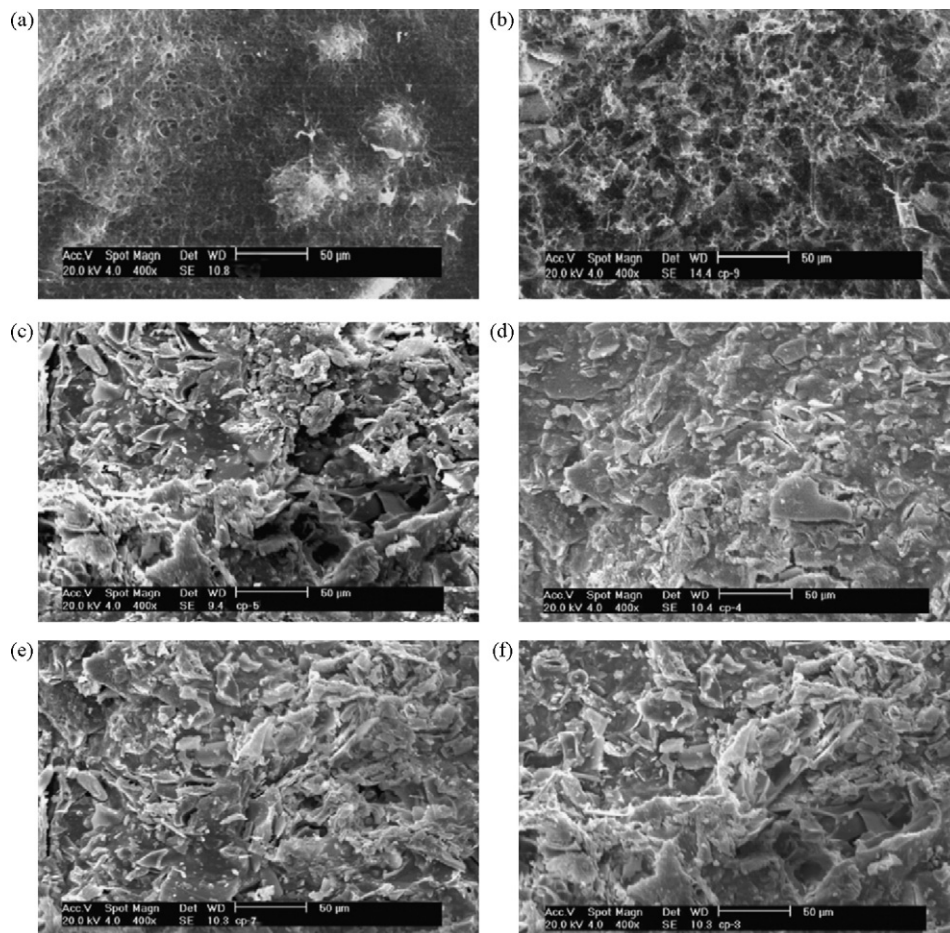


**Fig. 3.** SEM of: (a) outer surface of chitosan-coated perlite bead, (b) cross-section of chitosan-coated perlite bead, (c) after adsorption of Cu (II) and Ni (II), (d) after adsorption of Cu (II) and Co (II), (e) after adsorption of Ni (II) and Co (II) and (f) after adsorption of Cu (II), Co (II) and Ni (II).
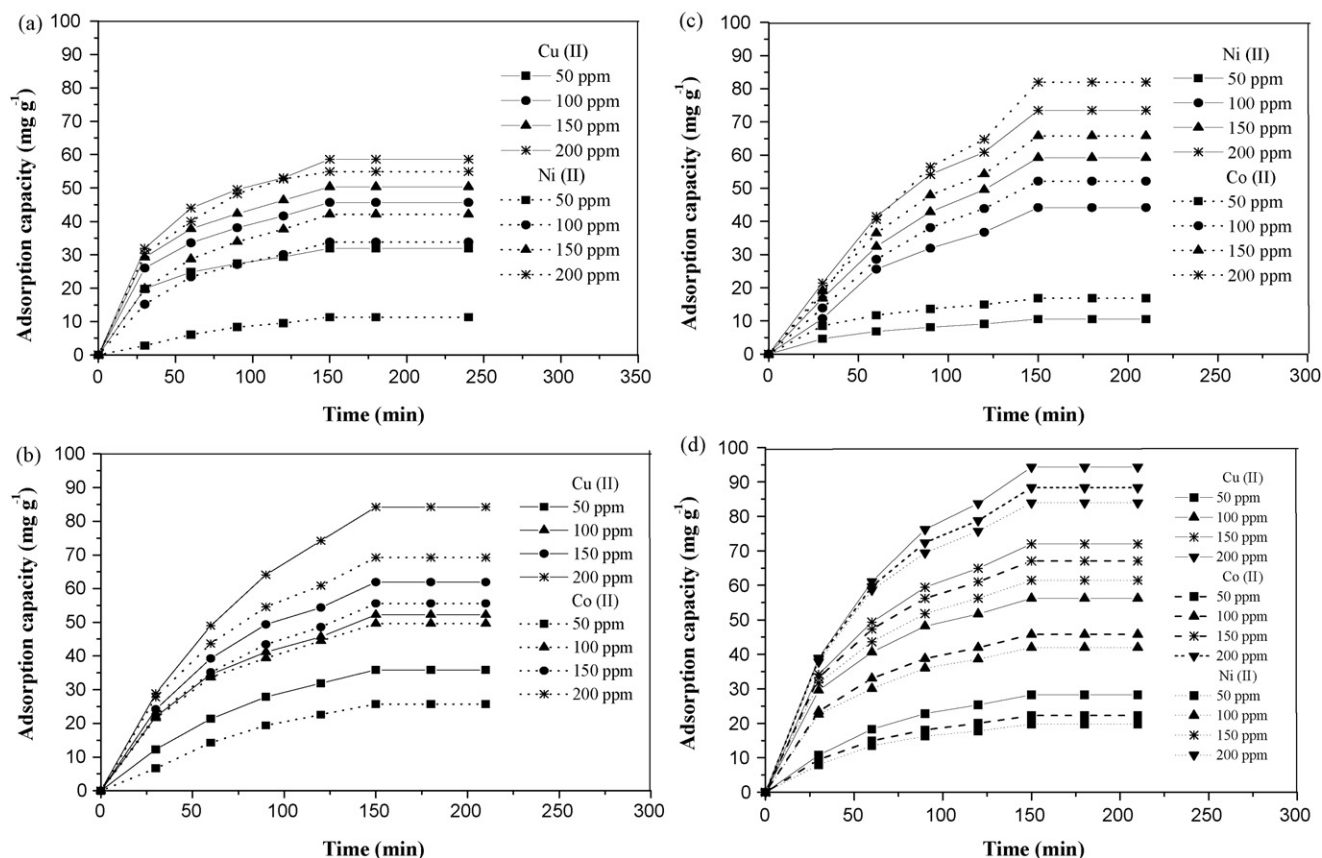
**Fig. 4.** Effect of agitation time on adsorption of: (a) Cu (II) and Ni (II), (b) Cu (II) and Co (II), (c) Ni (II) and Co (II) from bisolute solutions and (d) Cu (II), Co (II) and Ni (II) from trisolute solution on chitosan-coated perlite beads at different initial concentrations.

It can be observed that there is a change in the morphology of the beads after adsorption.

### 3.6. Contact time and sorption kinetics

Process performance and ultimate cost of an adsorption system depend upon the effectiveness of the process design and the efficiency of process operation. Metal uptake with CCP beads was positively correlated with increasing metal ion concentrations. The kinetics of adsorption of binary solutions of Cu (II) and Ni (II), Cu (II) and Co (II), and Ni (II) and Co (II) and trisolute solution of Cu (II), Co (II), and Ni (II) ions at different initial concentrations (50–200 ppm) by CCP beads at room temperature. Results from the Fig. 4a–d indicate that the adsorption capacity increases with an increase in the contact time before equilibrium was reached, which indicates that the metal ion removal by adsorption on CCP was concentration dependent. Other parameters such as dose of the adsorbent, pH of the solution and agitation speed were kept constant. Optimum contact time for all the metal ions in their bisolute solutions was found to be 150 min. Hence the CCP require a shorter contact time due to the availability of various functional groups on the surface of chitosan which were required for interaction with anions and cations, thus significantly improved the binding capacity and the process proceed rapidly [37]. The rate constant of adsorption of binary and tertiary metal solution on CCP was determined using a simple first order Lagergren's equation.

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_{ad}}{2.303}\right) t \qquad (2)$$

where $q_e$ was the amount of sorbate adsorbed per unit weight of sorbent at equilibrium ($mg\,g^{-1}$), $q_t$ was the amount of sorbate uptake per unit weight of sorbent at any time $t$ ($mg\,g^{-1}$), $t$ was

the time in minutes and $K_{ad}$ was the rate constant of adsorption. The values of $K_{ad}$ were calculated from the slopes of the plot of $\log(q_e - q_t)$ versus $t$ for different concentrations and the values of these constants were given in Table 1. From this observation it was concluded that the adsorption process from bisolute and trisolute solutions follows first order kinetics.

### 3.7. Effect of pH

The pH of the aqueous solution was an important variable, which controls the adsorption of the metals on the solid–water interfaces. The pH affects the availability of metal ions in solution and the metal binding sites of the adsorbent [38]. The effect of hydrogen ion concentration on the extent of adsorption was studied by varying pH of the solution from 3 to 8. Separate experiments were conducted to study the competitive adsorption characteristics of Cu (II) and Ni (II), Cu (II) and Co (II), and of Ni (II) and Co (II) from their of binary solute and Cu (II), Co (II) and Ni (II) trisolute solutions with constant initial concentration of each metal ion at 100 ppm which were in contact with 100 mg of sorbent and allowed to reach equilibrium. The equilibrium concentration of each metal ion was determined and the amount adsorbed per unit weight of sorbent at different pH values was determined. These results were graphically represented in Fig. 5a–d. The results indicate that the extent of adsorption varies with pH. Under acidic conditions (below pH 3) the chitosan undergoes dissolution [39]. Due to this dissolution, experiments were conducted above pH 3. From the figures it can be shown that there was an increase in metal uptake with an increase in pH up to 5.0. Higher pH values (above 5.0) results in the formation of metal hydroxide precipitates due to the presence of copper. But in case of Ni (II) and Co (II) bisolute solution, increase in pH results
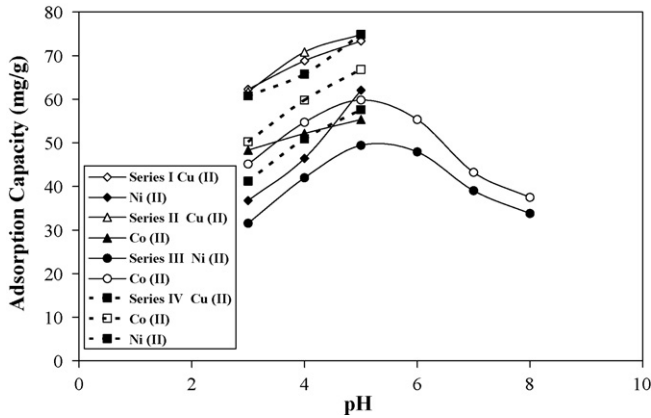
**Table 1**
Adsorption rate constants of Lagergren plots for Cu (II), Co (II) and Ni (II) bisolute and trisolute solution on chitosan-coated perlite beads.

| Bisolute solutions | Metal ions | Lagergren constants | Initial metal ion concentration (ppm) | | | |
|---|---|---|---|---|---|---|
| | | | 50 | 100 | 150 | 200 |
| Cu (II) and Ni (II) | Cu (II) | $K_{ad}$ | 0.0172 | 0.0175 | 0.0179 | 0.0172 |
| | | $R^2$ | 0.9973 | 0.9952 | 0.9914 | 0.997 |
| | Ni (II) | $K_{ad}$ | 0.0175 | 0.0175 | 0.0177 | 0.0177 |
| | | $R^2$ | 0.9995 | 0.9971 | 0.9978 | 0.9952 |
| Cu (II) and Co (II) | Cu (II) | $K_{ad}$ | 0.0198 | 0.0170 | 0.0179 | 0.0179 |
| | | $R^2$ | 0.9937 | 0.9992 | 0.9992 | 0.9987 |
| | Co (II) | $K_{ad}$ | 0.0198 | 0.0184 | 0.0172 | 0.0188 |
| | | $R^2$ | 0.9953 | 0.9931 | 0.9993 | 0.991 |
| Ni (II) and Co (II) | Ni (II) | $K_{ad}$ | 0.0152 | 0.0163 | 0.0163 | 0.0158 |
| | | $R^2$ | 0.9988 | 0.9957 | 0.9991 | 0.9987 |
| | Co (II) | $K_{ad}$ | 0.0161 | 0.0170 | 0.0156 | 0.0147 |
| | | $R^2$ | 0.9997 | 0.9996 | 0.9995 | 0.9985 |
| Trisolute solution Cu(II) + Co(II) + Ni(II) | Cu (II) | $K_{ad}$ | 0.02 | 0.02 | 0.0186 | 0.0186 |
| | | $R^2$ | 0.995 | 0.9985 | 0.999 | 0.999 |
| | Co (II) | $K_{ad}$ | 0.0193 | 0.0195 | 0.0191 | 0.0184 |
| | | $R^2$ | 0.9993 | 0.9997 | 0.9995 | 0.9993 |
| | Ni (II) | $K_{ad}$ | 0.0195 | 0.0198 | 0.0195 | 0.0191 |
| | | $R^2$ | 0.9992 | 0.9959 | 0.998 | 0.9998 |

in increase in adsorption capacity up to 5.0, and then decreases up to pH 8; thereafter these metal ions also get precipitated as their hydroxides. Adsorption of Cu (II) and Ni (II), Cu (II) and Co (II), and of Ni (II) and Co (II) from aqueous bisolute and their trisolute solutions exhibits competition for available adsorption surface sites. Copper was more strongly attracted to the sorbent, with higher removal percentages at the same pH than the other two metals that were scarcely affected by the presence of the other competitive metal in their solutions.

### 3.8. Effect of adsorbent dose

Quantity of biomass can influence the extent of metal uptake from solution. The dependence of metal ion sorption on dose was studied by varying the amount of adsorbents from 0.05 to 0.5 g, while keeping the volume (100 ml) and concentration (100 ppm) of the solution constant. The results were graphically represented in Figs. 6a–d. From the figures it can be noted that Cu (II) can



Fig. 5. Effect of pH on adsorption of: (a) Cu (II) and Ni (II), (b) Cu (II) and Co (II), (c) Ni (II) and Co (II) from bisolute solutions and (d) Cu (II), Co (II) and Ni (II) from trisolute solution on chitosan-coated perlite beads.
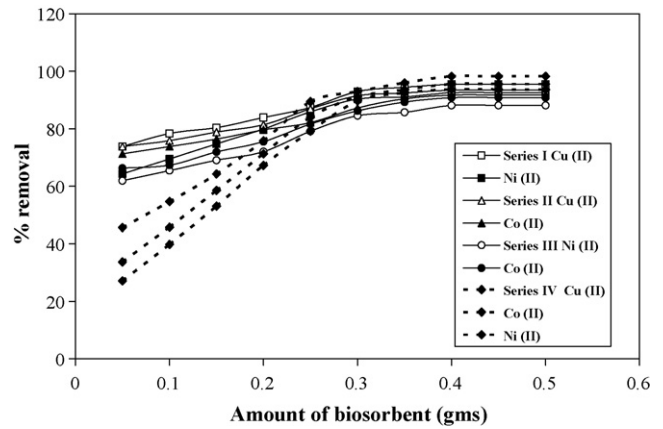


Fig. 6. Effect of dose of adsorbent (CCP beads) on percent removal of: (a) Cu (II) and Ni (II), (b) Cu (II) and Co (II), (c) Ni (II) and Co (II) from bisolute solutions and (d) Cu (II), Co (II) and Ni (II) from trisolute solution.

**Table 2**
Parameters of Langmuir and Freundlich isotherms for adsorption of Cu (II), Co (II) and Ni (II) from bisolute and trisolute solution on chitosan-coated perlite beads.

| Bisolute solutions | Metal ions | Langmuir constants | | | Freundlich constants | | |
|---|---|---|---|---|---|---|---|
| | | $Q^0$ | $b$ | $R^2$ | $K_F$ | $n$ | $R^2$ |
| Cu (II) and Ni (II) | Cu (II) | 147.05 | 0.0076 | 0.9978 | 1.422 | 1.158 | 0.9916 |
| | Ni (II) | 38.91 | 0.0171 | 0.9995 | 1.158 | 1.423 | 0.9912 |
| Cu (II) and Co (II) | Cu (II) | 156.25 | 0.0053 | 0.9955 | 1.064 | 1.140 | 0.9759 |
| | Co (II) | 39.84 | 0.0180 | 0.9983 | 1.208 | 1.425 | 0.9844 |
| Ni (II) and Co (II) | Ni (II) | 56.18 | 0.0151 | 0.9979 | 1.235 | 1.303 | 0.9934 |
| | Co (II) | 66.66 | 0.0143 | 0.9995 | 1.366 | 1.288 | 0.9967 |
| Trisolute solution Cu(II) + Co(II) + Ni(II) | Cu (II) | 128.20 | 0.0120 | 0.9975 | 1.791 | 1.152 | 0.9936 |
| | Co (II) | 35.211 | 0.0217 | 0.9978 | 1.300 | 1.474 | 0.9913 |
| | Ni (II) | 30.487 | 0.0166 | 0.9960 | 1.394 | 1.321 | 0.9924 |

**Table 3**
Maximum capacity, $Q^0$ (mg g$^{-1}$) for Adsorption of Cu (II), Ni (II) and Co (II) by various chitosan in its natural form and most of the modified forms.

| Adsorbent | Maximum adsorption capacity (mg g$^{-1}$) | | | pH | References |
|---|---|---|---|---|---|
| | Cu (II) | Ni (II) | Co (II) | | |
| Chitosan | 16.8 | 2.4 | – | 5.0 | [42] |
| Chitosan acetate crown ether (CCTS–1) | 23.9 | 0.7 | – | 5.6 | [43] |
| Chitosan diacetate crown ether (CCTS–2) | 31.3 | 4.1 | – | 5.6 | [43] |
| Epichlorohydrine cross-linked chitosan (CCTS) | 16.8 | 6.4 | – | 5.6 | [43] |
| Chitosan-coated PVC | 87.9 | 120.5 | – | 4.0–5.0 | [44] |
| Thiourea-modified magnetic chitosan microspheres (TMCS) | 66.7 | 15.3 | – | 6.0 and 7.0 | [45] |
| Chitosan | 1.584 | – | 1.260 | 6.0–8.0. | [46] |
| Chitosan | 80.71 | – | – | 6.0 | [47] |
| Chitosan-GLA beads | 59.67 | | | | |
| Chitosan-ECH beads | 62.47 | | | | |
| Chitosan-EGDE beads | 45.94 | | | | |

be adsorbed more selectively on CCP beads than Co (II) and Ni (II). Therefore, the order of affinity based on adsorption capacity, was Cu (II) > Co (II) > Ni (II) in bisolute as well as trisolute solutions studied. Adsorption of each single ion was reduced by the presence of other ion, which competes for some of the same active sites of the biosorbent [40]. It can be seen that the rate of removal of metal ions increases with the increase in the dose of adsorbent. There was a substantial increase in adsorption when the dose of adsorbents was increased from 0.05 to 0.4 g. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions.

### 3.9. Adsorption isotherms

Among various plots employed for analyzing the nature of adsorbate–adsorbent interaction, adsorption isotherm was the most significant. The results of adsorption studies of binary and tertiary mixtures of Cu (II), Co (II) and Ni (II) at different concentrations ranging from 10 to 100 ppm on a fixed amount of adsorbent were expressed by two of the most popular isotherm theories viz., Freundlich and Langmuir isotherms. These isotherm equations were as follows:

$$\text{Freundlich}: \quad \log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$
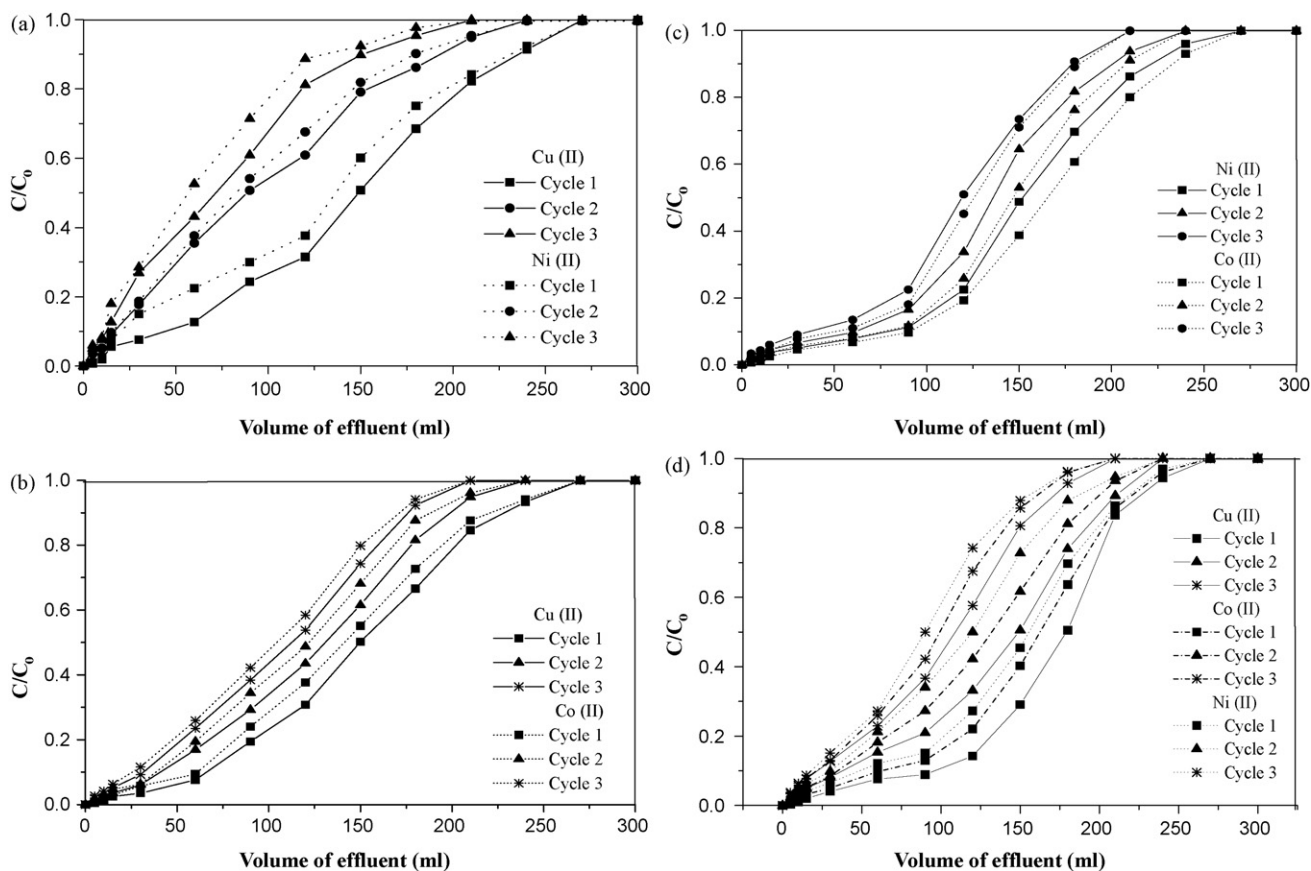


**Fig. 7.** Column break-through curves for adsorption of: (a) Cu (II) and Ni (II), (b) Cu (II) and Co (II), (c) Ni (II) and Co (II) from bisolute solution and (d) Cu (II), Co (II) and Ni (II) from trisolute solution on chitosan-coated perlite beads.
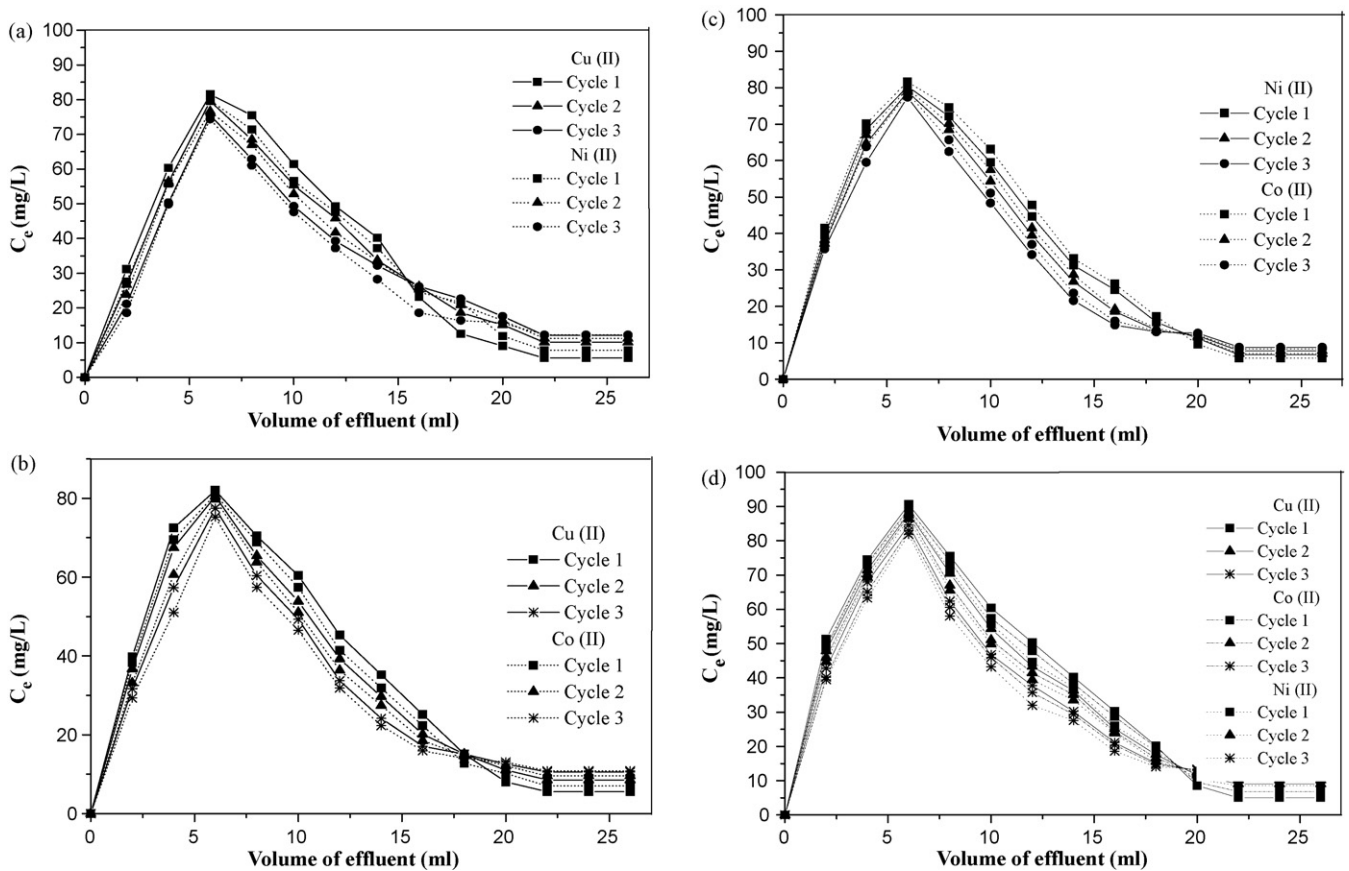
**Fig. 8.** Regeneration curves of chitosan-coated perlite beads loaded with (a) Cu (II) and Ni (II), (b) Cu (II) and Co (II), (c) Ni (II) and Co (II) from bisolute solution and (d) Cu (II), Co (II) and Ni (II) from trisolute solution.

Langmuir : $\quad \dfrac{1}{q_e} = \dfrac{1}{Q^0 b c_e} + \dfrac{1}{Q^0}$ (4)

In the above equations, $K_F$ and $n$ were Freundlich constants, which affect the adsorption process, such as adsorption capacity and intensity of adsorption, respectively. The values of these constants, obtained by least square fitting of the data on $\log q_e$ and $\log C_e$, $Q^0$ (mg g$^{-1}$) and $b$ were Langmuir constants related to monolayer adsorption capacity and energy of adsorption, respectively. 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. Adsorption capacities of chitosan and modified chitosan sorbents collected from the literature are included in Table 3 along with the values corresponding to CCP. The sorbent developed in the present study exhibits higher adsorption capacity compared to chitosan in its natural form and most of the modified forms.

### 3.10. Column adsorption and desorption studies

The experimental results, expressed typically with the break through curve concept, i.e., treated volume versus breakthrough (ratio of the column outlet concentration to the initial metal concentration, $C_{outlet}/C_{inlet}$) were presented in Fig. 7a–d. All these experiments were performed by passing the bisolute and trisolute solutions individually having optimal pH 5 through fixed bed columns loaded with 1 g of CCP beads at room temperature in a down flow-operating mode using a volumetric flow rate of 1 ml min$^{-1}$. The data were calculated by determining the con-

centration of individual metal ions at different time intervals in the effluent. The amount of solute adsorbed follows the order: Cu (II) > Co (II) > Ni (II). The order indicates that Cu (II) was more favorable solute for adsorption than Co (II) and Ni (II). In bisolute and trisolute adsorption, it was observed that the extent of adsorption of one component decreases in the presence of other. The effect was more in case of Ni (II) adsorption in the presence of Cu (II) or Co (II). The adsorption bed was considered to be exhausted when concentration of the effluent coming out of the column reached the allowable maximum discharge level.

Desorption of metals deposited on the biosorbent was not only possible but the determination of its dynamics represents a crucial information for biosorption process designed and for metal recovery feasibility assessment [41]. Cu (II), Co (II) and Ni (II) from the loaded CCP beads with bisolute and trisolute components were desorbed by using 0.1N NaOH solution as an eluent at the rate of 1 ml min$^{-1}$. NaOH was used as a solvent of choice because of its solubility parameters and solvation forces of NaOH overweigh the attractive forces of CCP for metal ions. Desorption of these divalent metal ions from CCP was believed to be mainly due to deprotonation of chitosan amine groups above pH 10. Due to this, metal ions migrate from adsorbed state to solvent phase. The plots between the volumes of eluent solvent collected and concentration of solute in the eluent for bisolute and trisolute solutions of Cu (II), Co (II) and Ni (II) were given in Fig. 8a–d. Maximum desorption occurs within 6 ml of alkali effluent. In this process the concentration of solute in the first collected eluent solvent was low, then increases sharply and thereby decreases in the subsequent volumes.

## 4. Conclusion

Chitosan was effectively coated on an inert substrate, perlite and was made in the form of spherical beads. In this study adsorption of Cu (II), Ni (II) and Co (II) from their binary and tertiary solute solutions on chitosan-coated perlite has been investigated through batch and column studies. EDXRF, FTIR studies of beads that were exposed to metal solution indicated that amine and hydroxy groups were the main adsorption sites for the metal ions. Surface area analysis studies of chitosan-coated adsorbent showed highly porous nature. The adsorption of metal ions was heavily dependent on the amount of adsorbent, concentration of metal ions, agitation time and pH of the metal solution. Maximum removal of Cu (II), Ni (II) and Co (II) on chitosan-coated on perlite was at pH 5.0. The equilibrium adsorption data were correlated by Langmuir and Freundlich isotherm equations. Rate constants for adsorption were calculated from the Lagergren's equation. Consequently, chitosan biosorption technologies were still being developed and much more work was required. Some practical applications have been achieved, and the fundamentals look promising: chitosan have the potential to remove metal ions to very low concentration and to accumulate large amounts of specific toxic elements. But, very little comparative or comparable information, especially economical analysis, was available.

## References

[1] A. Demirbas, Heavy metal adsorption onto agro-based waste materials, J. Hazard. Mater. 157 (2008) 220–229.

[2] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. saini, Removal of cadmium and nickel from waste water using bagasses and flyash—a sugar industry waste, Water Res. 37 (16) (2003) 4038–4044.

[3] A.E. Sikaily, A.E. Nemr, A. Khaled, O. Abdelwehab, Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon, J. Hazard. Mater. 148 (2007) 216–228.

[4] V.K. Gupta, Equilibrium uptake, sorption dynamics, process development and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag-a low cost adsorbent, Ind. Eng. Chem. Res. (ACS) 37 (1998) 192–202.

[5] V.K. Gupta, V.K. Saini, N. Jain, Adsorption of As (III) from aqueous solutions by iron-oxide coated sand, J. Colloid Interface Sci. 288 (2005) 55–60.

[6] V.K. Gupta, D. Mohan, S. Sharma, Removal of lead from wastewater using bagasse flyash—a sugar industry waste material, Sep. Sci. Technol. 33 (9) (1998) 1331–1343.

[7] S. Wang, H. Wu, Environmental-benign utilisation of fly ash as low-cost adsorbents, J. Hazard. Mater. 136 (2006) 482–501.

[8] V.K. Gupta, S. Sharma, Removal of zinc from aqueous solutions using bagasse flyash - a low cost adsorbent, Ind. Engg. Chem. Res. 42 (25) (2003) 6619–6624.

[9] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse flyash—a sugar industry waste, J. colloid Interface Sci. 271 (2004) 321–328.

[10] A.H. Oren, A. Kaya, Factors affecting adsorption characteristics of $Zn^{2+}$ on two natural zeolites, J. Hazard. Mater. 131 (2006) 59–65.

[11] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review, Bioresour. Technol. 99 (14) (2008) 6017–6027.

[12] V.K. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminum industry waste, Water Res. 35 (5) (2001) 1125–1134.

[13] V.K. Gupta, S. Sharma, Removal of cadmium and zinc from aqueous solutions using red mud, Environ. Sci. Technol. 36 (16) (2002) 3612–3617.

[14] S.P. Singh, L.Q. Ma, M.J. Hendry, Characterization of aqueous lead removal by phosphatic clay: equilibrium and kinetic studies, J. Hazard. Mater. 136 (2006) 654–662.

[15] C. Chen, J. Wang, Removal of $Pb^{2+}$, $Ag^+$, $Cs^+$ and $Sr^{2+}$ from aqueous solution by brewery's waste biomass, J. Hazard. Mater. 151 (1) (2008) 65–70.

[16] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.

[17] V.K. Gupta, A. Rastogi, Equilibrium and kinetic modeling of cadmium (II) biosorption by non-living algal biomass *Oedogonium* sp. from aqueous phase, J. Hazard. Mater. 153 (2008) 759–766.

[18] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by non-living algal biomass *Oedogonium* sp. and *Nostoc* sp.—a comparative study, Colloid Surfaces B 64 (2) (2008) 170–178.

[19] V.K. Gupta, A.K. Srivastava, N. Jain, Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species, Water Res. 35 (2001) 4079–4085.

[20] V.K. Gupta, A. Rastogi, V.K. Saini, N. jain, Biosorption of copper (II) from aqueous solutions by *Spirogyra* species, J. Colloid Interface Sci. 296 (2006) 59–63.

[21] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilbrium studies, J. Hazard. Mater. 152 (2008) 407–414.

[22] V.K. Gupta, A. Rastogi, Sorption and desorption studies of chromium (VI) from non viable cyanobacterium Nostoc muscorum biomass, J. Hazard. Mater. 154 (2008) 347–354.

[23] N.S. Krishnan, A.K. Sharma, R. Sanghi, Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater, J. Hazard. Mater. 148 (2007) 353–359.

[24] D. Zhou, L. Zhang, S. Guo, Mechanisms of lead biosorption on cellulose/chitin beads, Water Res. 39 (2005) 3755–3762.

[25] C. Jeon, K.H. Park, Adsorption and desorption characteristics of mercury (II) ions using aminated chitosan bead, Water Res. 39 (2005) 3938–3944.

[26] N. Kuyucak, B. Volesky, Biosorbents for recovery of metals from industrial solutions, Biotechnol. Lett. 10 (1988) (1988) 137–142.

[27] C. Jeon, W.H. Holl, Application of the surface complexation model to heavy metal sorption equilibria on to aminated chitosan, Hydrometallurgy 71 (2004) 421–428.

[28] T.W. Tan, X.J. He, W.X. Du, Adsorption behavior of metal ions on imprinted chitosan adsorbent, J. Chem. Technol. Biotechnol. 76 (2001) 191–195.

[29] R.S. Juang, C.Y. Ju, Kinetics of sorption of Cu (II)-ethylenediaminetetraacetic acid chelated anions on cross-linked, polyaminated chitosan beads, Ind. Eng. Chem. Res. 32 (1998) 386.

[30] V.M. Boddu, A. Krishnaiah, L.T. Jonathan, E.D. Smith, Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent, Environ. Sci. Technol. 37 (2003) 4449–4456.

[31] S.M. Nomanbhay, K. Palanisamy, Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal, Electron. J. Biotechnol. 8 (2005) 43–53.

[32] S. Kalyani, A. Krishnaiah, V.M. Boddu, Adsorption of divalent cobalt from aqueous solution onto chitosan-coated perlite beads as biosorbent, Sep. Sci. Technol. (2007) 2767–2786, http://www.informaworld.com/smpp/title~content= t713708471~db=all~tab=issueslist~branches=42 - v4242.

[33] A. Findon, G. McKay, H.S. Blair, Transport studies for the sorption of copper ions by chitosan, J. Environ. Sci. Heal A 28 (1993) 173–185.

[34] V.W.D. Chui, K.W. Mok, C.Y. Ng, B.P. Luong, K.K. Ma, Removal and recovery of copper (II), chromium (III), and nickel (II) from solutions using crude shrimp chitin packed in small columns, Environ. Int. 22 (1996) 463–468.

[35] J. Lerivrey, B. Dubois, P. Decock, J. Micera, J. Kozlowski, Formation of D-glucosamine complexes with Cu(II), Ni(II) and Co(II) ions, Inorg. Chim. Acta 125 (1986) 187–190.

[36] K. Inoue, K. Yoshizuka, K. Ohto, Adsorptive separation of some metal ions by complexing agent types of chemically modified chitosan, Anal. Chim. Acta 388 (1999) 209–218.

[37] S. Hasan, A. Krishnaiah, T.K. Ghosh, V.M. Boodu, E.D. Smith, Chromium (VI) adsorption capacity of chitosan coated on an inert substrate perlite, Sep. Sci. Technol. 38 (2003) 3375–3393.

[38] A.I. Zouboulis, K.A. Matis, M. Loukidou, F. Sebesta, Metal biosorption by PAN-immobilized fungal biomass in simulated wastewaters, Coll. Surf. A 212 (2003) 185–196.

[39] S. Kalyani, J. Ajitha Priya, P. Srinivasa Rao, A. Krishnaiah, Removal of copper and nickel from aqueous solutions using chitosan coated on perlite as biosorbent, Sep. Sci. Technol. 40 (2005) 1483–1495.

[40] R.L. Ramos, L.A.B. Jacome, R.M.G. Coronado, L.F. Rubio, Competitive adsorption of Cd (II) and Zn (II) from aqueous solution onto activated carbon, Sep. Sci. Technol. 36 (2001) 3673–3687.

[41] D. Kratochvil, B. Volesky, G. Demopoulos, Optimizing Cu removal/recovery in a biosorption column, Water Res. 31 (1997) 2327–2339.

[42] C. Huang, Y.C. Chung, M.R. Liou, Adsorption of Cu(II) and Ni(II) by pelletized biopolymer, J. Hazard. Mater. 45 (1996) 265–277.

[43] S. Tan, Y. Wang, C. Peng, Y. Tang, Synthesis and adsorption properties for metal ions of crosslinked chitosan acetate crown ethers, J. Appl. Polym. Sci. 71 (1999) 2069–2074.

[44] P. Srinivasa Rao, Y. Vijaya, V.M. Boddu, A. Krishnaiah, Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads, Bioresour. Technol. 100 (2009) 194–199.

[45] L. Zhou, Y. Wang, Z. Liu, Q. Huang, Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres, J. Hazard. Mater. 161 (2009) 995–1002.

[46] R.B. da Silva, A.F.L. Neto, L.S.S. dos Santos, J.R. de Oliveira Lima, M.H. Chaves, J.R. dos Santos Jr., G.M. de Lima, E.M. de Moura, C.V.R. de Moura, Catalysts of Cu(II) and Co(II) ions adsorbed in chitosan used in transesterification of soy bean and babassu oils—a new route for biodiesel syntheses, Bioresour. Technol. 99 (2008) 6793–6798.

[47] W.S. Wan Nggah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, React. Funct. Polym. 50 (2002) 181–190.