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Removal of Copper (II) and Nickel (II) Ions from Aqueous Solutions by a Composite Chitosan Biosorbent

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Abstract: A composite chitosan biosorbent (CCB) was prepared by coating chitosan on to ceramic alumina. The adsorption characteristics of the sorbent for copper and nickel ions were studied under batch equilibrium and dynamic flow conditions at pH 4.0. The equilibrium adsorption data were correlated with Langmuir, Freundlich, and Redlich-Peterson models. The ultimate monolayer capacities, obtained from Langmuir isotherm, were 86.2 and 78.1 mg/g of chitosan for Cu(II) and Ni(II), respectively. In addition, dynamic column adsorption studies were conducted to obtain breakthrough curves. After the column was saturated with metal ions, it was regenerated with 0.1 M sodium hydroxide. The regenerated column was used for a second adsorption cycle.

Keywords: Adsorption, chitosan, copper (II), nickel (II), adsorption isotherms

INTRODUCTION

Dissolution of copper from domestic plumbing contributes the greatest proportion of copper in domestic effluents, which in turn contributes, between

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60 and 90% of the copper load entering non-industrialized sewage treatment works. This increase in copper load should be considered in the context of more stringent standards for the release of copper to the environment. In addition, copper is used in metal plating, brake linings, engine moving parts, bearing and bushing ware, fungicides, and insecticides. When the concentration of copper reaches the action level (1.3 mg/L), the public water supplier is required to carry out water treatment. Though we require about 1000 micrograms of copper in our diet every day, at elevated levels, however, copper can cause nausea, vomiting, diarrhea, and stomach cramps. Infants under one year of age can sustain permanent kidney and liver damage if they suffer long-term exposure (more than 14 days) to elevated levels of copper. Nickel is used to make stainless steel and other metal alloys. The most common problem of nickel is its effect on skin (dermal) in people who are sensitive to the metal. Workers who have inhaled very large amounts of nickel compounds have developed lung and nasal sinus cancers. Nickel compounds are also used in nickel-plating, coloring ceramics, manufacturing batteries, and as catalysts. Much of the nickel in the environment is found in soil and sediments. Nickel attaches to particles that contain iron or manganese, which are often present in soil and sediments.

Owing to their adverse effects on human health, 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 the aquatic environment. These methods have inherent advantages and limitations. Chitosan, in its natural and modified forms, has been used extensively as an adsorbent to treat water contaminated with toxic metals. Often the specific binding sites of the chitosan in its natural form are not readily available for sorption, and the chitosan has a tendency to agglomerate or form gels. It is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. A number of attempts have been made to synthesize adsorbents based on chitosan and to study their adsorption capacity for copper and nickel. Kawamura et al. (1) studied the adsorption of Cu (II) and Ni (II) on polyaminated, highly porous, chitosan chelating resin along with the other trace metals. Kondo et al. (2, 3) examined the adsorption characteristics of metal ions on a novel chitosan-supported sulfonic acid resin modified by propane sultone and galactose. Chitosan pellets (4) were used to remove copper and nickel from polluted water. 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 (5). Ni and Xu (6) synthesized a series of resins based on chitosan and investigated adsorption capacity, rate, and selectivity for different metal ions. Wan Ngah et al. (7) have studied the removal of Cu (II) from aqueous solutions using chitosan, and chitosan cross-linked with glutaraldehyde, epichlorohydrin, and ethylene glycol diglycidyl ether. Juang et al. (8) investigated the adsorption removal of Cu (II) ions from simulated rinse solutions containing several chelating agents using chitosan. EDTA- and DTPA-chitosan (9) and amidoxime chitosan resin (10) were prepared and the adsorption characteristics for Cu (II) and Ni (II) ions were examined. Tseng et al. (11) studied the effect of the degree of deacetylation and the source of chitosan on the adsorption ability for Cu (II) and Ni (II) ions. 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. (12). Cross-linked chitosan acetate crown ethers (13) and grafted chitosan diamine crown ethers (14) were synthesized and evaluated for the adsorption capacity for different metal ions. Schmuhl et al. (15) studied the adsorption capacity of cross-linked and non-cross-linked chitosan for Cu (II) and Cr (VI) ions. Nickel imprinted chitosan resin (16) and cross-linked chitosan with copper as the template (17) were prepared to improve the adsorption capacity and selectivity for trace metal ions. Guibal (18) reported that chitosan is very efficient at sorbing metal cations by chelation at near neutral pH and metal anions by electrostatic attraction to protonated amine groups in acidic solutions. Varma et al. (19) reviewed various classes of chitosan derivatives and compared their ion binding abilities under varying conditions, as well as the analytical methods of analysis, the sorption mechanisms, and structural analysis of the metal complexes by various methods. Khazali et al. (20) have investigated the removal of Cu (II) from aqueous solutions by Jordanian pottery materials. Shameem et al. have studied the adsorption of hexavalent chromium (21) and divalent cadmium (22) and Kalyani et al. (23) have investigated the removal of divalent copper and nickel ions from water using chitosan coated perlite. With an objective to provide a physical support to withstand the mechanical pressure in a hydrodynamic environment, to improve its resistance towards dissolution in acidic medium, to make the binding sites readily available for the adsorbate and to increase the porosity thereby to achieve enhanced adsorption rates, we have prepared a composite chitosan biosorbent by coating chitosan-oxalic acid gel on alumina (24). The characterization of the CCB and evaluation of adsorption capacity for Cr (VI) were reported in our earlier communication (25). The primary objective of the present study was to evaluate the removal efficiency of the CCB for Cu (II) and Ni (II) ions from aqueous solutions. This was accomplished by studying the adsorption characteristics of Cu (II) and Ni (II) ions on the CCB in batch equilibrium and column dynamic conditions at pH 4.0. Further, the adsorbent loaded with metal ions was regenerated with sodium hydroxide solution and the regenerated bed was used for a second adsorption cycle to test its mechanical integrity and sorption capacity.

EXPERIMENTAL

Materials

Medium molecular weight chitosan (75–85% deacetylated), oxalic acid dehydrate, and 150 mesh-activated alumina were obtained from Sigma-Aldrich Chemicals (St. Louis, MO, USA). Cupric (II) chloride dihydrate was obtained from J. T. Baker, and Nickel (II) sulfate was obtained from Chem Service. Sodium hydroxide was purchased from Fischer Chemicals. Stock solutions (1000 ppm) of Cu (II) and Ni (II) were prepared by dissolving appropriate amounts of $CuCl_2 \cdot 2H_2O$ and $NiSO_4$ respectively, in distilled deionized water. Solutions of lower concentrations were prepared by diluting the stock solutions. Multi-element stock standards (Spex Industries, Edison, NJ and VHG Labs, Manchester, NH) were used for preparation of analytical standards. Independent calibration check standard solutions were obtained either from separate lots of the calibration standards or from Sigma-Aldrich Chemicals (St. Louis, MO, USA). All calibration stock and independent stock standards were NIST traceable. ASTM Type I water (resistivity $>18\ M\Omega$, Labconoco, Kansas City, MO) was used throughout.

Synthesis of Chitosan Coated Biosorbent

Chitosan coated biosorbent was prepared by dip coating the ceramic substrate alumina with chitosan gel. The ceramic α-alumina (150 mesh) was dried in an oven for 4 hours at 110°C and mixed with 10 wt% oxalic acid and stirred for 18 hours at room temperature. The acid from the mixture was filtered, washed twice with DI water and dried at ~70°C under vacuum. About 50 grams of medium molecular weight chitosan was slowly added to 1000 ml of 10 wt% oxalic acid while stirring constantly with a magnetic stirrer. The acid and chitosan formed a viscous mixture and it was heated to 40–50°C for 3–4 hours to facilitate mixing. About 500 ml of the chitosan gel was diluted with water (~500 ml) and heated to 40–50°C while stirring vigorously. About 500 grams of the acid treated alumina was slowly added to the diluted gel and stirred for about 36 hours at constant stirring rate. The contents were allowed to settle and then filtered under vacuum. The filtered material (composite chitosan biosorbent) was washed twice with DI water and dried in the oven at 55°C under vacuum for 24 hours. Once-coated alumina was treated again with chitosan-oxalic acid gel (~500 ml) for 26 hours under constant stirring conditions. The mixture was allowed to settle. The supernatant liquid was decanted and the solid pasty material was treated with 1250 ml of 1 N NaOH. The alkaline mixture was stirred again for an hour. Later the mixture was filtered and washed with DI water until the filtrate was neutral. Twice-coated biosorbent was then allowed to dry in the oven under vacuum at 55°C for about 48 hours. The biosorbent was sieved and the beads between −32 and +60 mesh were used for the experimental work. The biosobent was characterized by

a. Pyrolysis
b. Porosimetry, and
c. Scanning Electron Microscopy,

as discussed earlier (26). Chitosan attaches to alumina through oxalic acid, which forms a bridge between alumina and chitosan. One carboxylate group of oxalic acid forms a surface chelate via ester linkage with the alumina while the other carboxylate group forms ionic (or electrostatic) bond with -NH_3^+ groups present in chitosan. The oxalic acid could also form hydrogen bonds with -OH, -CH_2OH, or -NH_2 groups on the biopolymer.

Analysis of Metal Ions

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (TJA Solutions, VG Excel, Franklin, MA), was used for determination of concentration of Cu (II) and Ni (II) ions. Quantitation was achieved by comparison of the pulse count rate (intensity) of the sample with that of various standards used to calibrate the instrument. The instrument was calibrated from 1 to 100 ng/ml. Fourier Transform Infrared (FTIR) spectra of biosorbent, and biosorbent adsorbed with copper and nickel ions were obtained using a JASCO Model 4100 spectrophotometer (Tokyo, Japan).

Batch Adsorption Experiments

Batch equilibrium adsorption isotherm studies were conducted with 100 ppm aqueous solutions of Cu (II) and Ni (II). The equilibrium isotherm measurements were carried out by keeping the solution volume and concentration constant while varying the amount of the added biosorbent in most of the cases. In some experiments the amount of biosorbent and the volume of the adsorbate were kept constant and the concentration of the metal ion solution was varied. The pH of the solutions was adjusted by adding 1.0 M sodium hydroxide or 1.0 M nitric acid solutions. The pH was measured using Beckman ϕ32 pH meter. The batch experiments were carried out at constant temperature in a shaking water bath at pH 4.0. We have chosen pH 4.0 for our studies in order to demonstrate that the CCB is stable in acidic medium though chitosan is soluble in solutions of pH less than 5.0. Temperature of the bath was maintained at 25 ± 0.5°C. The equilibration (shaking) time was 24 hours at an agitation speed of

200 rpm. The amount of biosorbent added to the solution was varied from 100–500 mg. After the isothermal equilibration, the biosorbent was separated by filtration with Whatman 41 filter paper. The filtrate was analyzed for metals. The amount of the metal adsorbed (mg) per unit mass of chitosan (g), q_e, was obtained by mass balance using the equation,

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where C_i and C_e are initial and equilibrium concentration of the metal ion (mg/L), m is dry mass of chitosan (g) present in the biosorbent and V is volume of the solution (L).

Column Adsorption Experiments

Dynamic flow adsorption experiments were conducted in a glass column of about 1.1 cm internal diameter and 30 cm length. The bed volume of the column was 30 cm^3. The column was fully jacketed to circulate water from a constant temperature water bath enabling the experiment to be carried out at constant temperature. The column had internal threads at both the ends to fit the adapters. Teflon O-rings were used to eliminate leakages. The adapters were fitted with polyethylene filter discs of 100-micron pore size. The adsorbent was washed thoroughly with water and dried prior to use. The column was packed with the dried adsorbent while shaking the column. This ensured that the maximum amount of adsorbent was packed without gaps. Then it was fixed to a perpendicular stand. The column was maintained at 25 ± 0.5°C by circulating water from a thermostat bath through the external jacket of the column. The influent solution was pumped from the reservoir into the column in an up-flow direction. The up flow mode of operation was chosen to avoid channeling of the influent solution. A constant flow rate was maintained throughout the run. The pH of the solution was adjusted to 4.0 by adding 1.0 M sodium hydroxide or 1.0 M nitric acid. It was observed that the adsorption capacity of CCB was not significantly affected by anions (23). The effluent solution was collected at different time intervals, and the concentration of the metal ions in the effluent solution was analyzed using the ICP-MS. The solutions were diluted appropriately prior to analysis. After the column was exhausted, it was regenerated using 0.1 M sodium hydroxide solution. Before the regeneration, the column was drained of the remaining aqueous solution by pumping air. Then the sodium hydroxide solution was pumped in to the column maintained at constant temperature and at a fixed flow rate. After the biosorbent was regenerated, the column was washed with about 200 ml DI water before introducing the influent solution for subsequent adsorption studies.

RESULTS AND DISCUSSION

Characteristics of Adsorbent

Pyrolysis of composite chitosan biosorbent at 750°C indicated that 21.07% of chitosan was present in the adsorbent. Surface area, average pore volume, and average pore diameter, determined with BET nitrogen porosimeter, were 105.2 m^2/g, 0.187 cm^3/g and 71.2 Å, respectively. Scanning electron micrographs (SEM) of the biosorbents, shown in Fig. 1, indicated the porous structure, spherical shape, and the approximate size of the particles (100–150 microns). FTIR spectra of sorbent before and after adsorption under wet conditions were recorded on FTIR spectrophotometer (Jasco, FT/IR-4100) in attenuated total reflectance (ATR) mode using ZnSe single reflection ATR plate (MIRacle^{TM} ATR, PIKE Technology). The FTIR spectra of the biosorbent as such and loaded with Cu (II) and Ni (II) are included in Figs. 2–4. The FTIR spectrum of CCB in Fig. 2 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 -NH_2), 1393.3 cm^{-1} (-NH deformation vibration in -NH_2), and 1065.5 cm^{-1} (-C-O-C-stretching). This reveals that all functional groups are intact even after coating on alumina and are available for interaction with the metal ions. FTIR spectra of CCB loaded with Cu (II) and Ni (II) along with those of the virgin CCB, shown in Figs. 3 and 4, exhibit a similar pattern indicating that both the metallic ions are adsorbed on CCB through the same mechanism. The intensity of transmittance of peaks is relatively greater in the case of CCB loaded with metal ions compared to the virgin CCB. This may be attributed to the presence of fewer free functional groups in the CCB loaded with metal ions. This observation provides evidence that the functional groups such as -NH_2, and -OH are involved in binding the

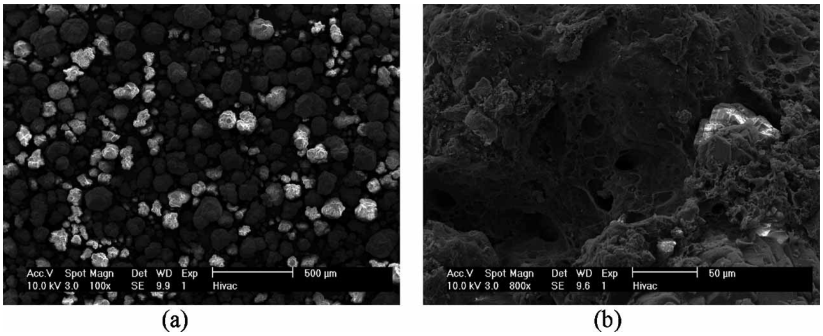

Figure 1. Scanning electron micrographs of the composite chitosan biosorbent at (a) 100X and (b) 800X.

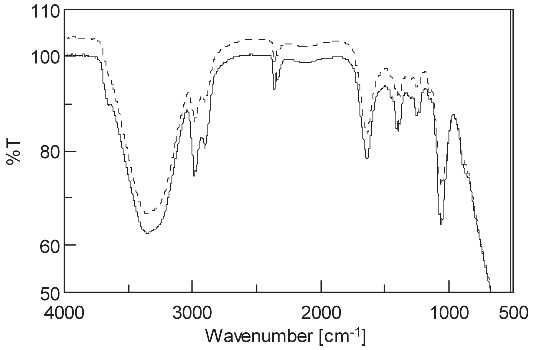

Figure 2. Composite chitosan biosorbent wet (dotted) and loaded with Ni (II) (solid).

metal ions to CCB. Formation of a complex between metal ions and CCB is shown in Fig. 4.

Equilibrium Adsorption

All the equilibrium experiments were performed at 25°C and pH 4.0. The equilibrium adsorption results for Cu (II) and Ni (II) on composite chitosan biosorbent are shown in Fig. 5. The plots in the figure show the adsorption isotherms are regular, positive, and concave to the concentration axis. Initially the adsorption is quite steep followed by a slow approach to equilibrium at higher adosrbate concentrations. These results demonstrate the potential use of the biosorbent for the removal of Cu (II) and Ni (II) from an aqueous medium over a wide concentration range. The uptake of metal ions is due to various processes such as adsorption, ion exchange and chelation. The evidence currently available supports the concept that

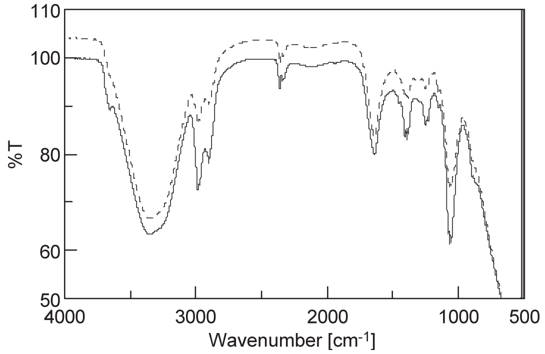

Figure 3. Composite chitosan biosorbent wet (dotted) and loaded with Cu (II) (solid).

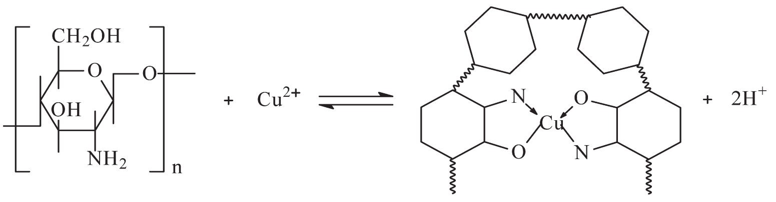

Figure 4. Formation of a complex between chitosan and divalent metal ion.

chitosan interacts with the metal ions primarily through the amino groups, which function as ligands (12, 26). Usually chelation requires the involvement of two or more complexing groups from the same molecule. The metal ion seeks amino groups from chitosan. The two amino groups involved may be from two glucosamine residues of the same polymer chain or two different polymer chains. The amino group in chitosan is considered to be the active site for metal ion adsorption due to the presence of a lone pair of electrons. In an acidic medium the amino group undergoes protonation and hence the metal ions have to compete with hydrogen ions for active sites. In addition to the amino group, the involvement of hydroxyl groups can not be ignored in complex formation. As seen in Fig. 5, the adsorption capacity of the sorbent decreases from Cu (II) to Ni (II). A similar trend was reported by Tseng et al. (27), Huang et al. (4), Inoue et al. (9), and Gupta (28).

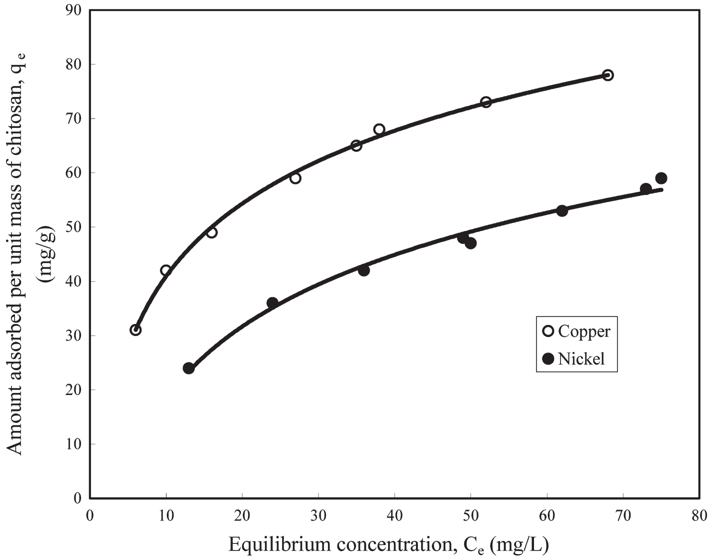

Figure 5. Equilibrium isotherms for adsorption of copper and nickel on composite chitosan biosorbent.

The higher adsorption capacity of the adsorbent for Cu (II) may be attributed to the presence of more empty atomic orbitals in copper.

Adsorption Isotherms

The amount of metal adsorbed per unit mass of adsorbent, q_e (mg/g), was correlated with the liquid phase concentration at equilibrium, C_e (mg/L), using Langmuir, Freundlich, and Redlich-Peterson adsorption isotherms. The Langmuir equation is,

$$q_e = \frac{Q^0 b C_e}{(1 + bC_e)} \tag{2}$$

where Q^0 (mg/g) and b (L/g) are the Langmuir constants. Q^0 is the amount of metal ions adsorption corresponding to monolayer coverage. The values of the parameters were evaluated from the linear plot of $1/q_e$ vs $1/C_e$. Freundlich adsorption isotherm is

$$q_e = kC_e^{1/n} \tag{3}$$

where k and n are constants for a given adsorbent-adsorbate system. The values of the constants were obtained from the linear plot of Log q_e vs Log C_e.

Redlich and Peterson (29) proposed a three-parameter adsorption model to improve the correlation of the experimental data. The equation takes the form,

$$q_e = \frac{K_1 C_e}{(1 + K_2 C_e^{\alpha})} \tag{4}$$

where K_1, K_2, and α are constants for a given adsorbent-adsorbate system. The three parameters in Equation (4) were obtained through a least squares fitting procedure by varying the value of α and minimizing the difference between the experimental and calculated data. The Redlich-Peterson plots are given in Fig. 6. The values of the constants of all the three models along with the regression coefficient (R^2) are listed in Table 1. All the adsorption models fit the experimental data well. Between the Langmuir and the Freundlich models, the Langmuir equation gives a better representation than that of Freundlich. Of course with three parameters α being an adjustable parameter, the Redlich-Peterson model gives a better fit among the three models. Although α has no exact physical significance, it was mentioned that α values between 0 and 1 indicate a favorable adsorption and the higher values of α may reflect a weaker interaction between adsorbent and adsorbate (27).

The Langmuir constant b, related to energy of adsorption, was used to evaluate the dimensionless parameter known as separation factor

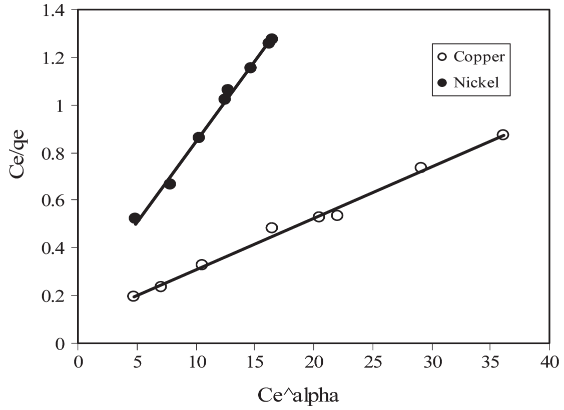

Figure 6. Redlich-Peterson isotherms for adsorption of copper and nickel on CCB. Alpha is 0.85 for copper and 0.65 for nickel.

(R_L) using the equation,

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the initial concentration of the metal ion (mg/L) and b is the Langmuir constant (L/mg). R_L values indicate whether the isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavorable ($R_L > 1$). The values of R_L calculated at different initial concentrations of Cu (II) and Ni (II), included in Table 2, indicate that the adsorption is favorable as the R_L values for both Cu (II) and Ni (II) at different initial concentration are between 0 and 1.

Table 1. Parameters of Langmuir, Freundlich, and Redlich-Peterson isotherms for adsorption of copper and nickel on composite chitosan biosorbent

Adsorption model	Parameters	Copper	Nickel
Langmuir	Q_0	86.21	78.13
	b	0.093	0.034
	R^2	0.9930	0.9940
Freundlich	K	16.96	7.23
	n	2.67	2.06
	R^2	0.9827	0.9876
Redlich-Peterson	K_1	10.63	6.21
	K_2	0.23	0.43
	α	0.85	0.65
	R^2	0.9993	0.9938

Table 2. Values of separation factor (R_L) at different initial concentrations of Cu (II) and Ni (II)

C_0	Cu(II)	Ni(II)
10	0.52	0.75
20	0.35	0.59
30	0.26	0.49
40	0.21	0.42
50	0.18	0.37
60	0.15	0.33
70	0.13	0.28
80	0.12	0.27
90	0.11	0.25
100	0.10	0.23

The maximum monolayer adsorption capacities of various adsorbents for copper and nickel ions from literature along with the results of the present study are included in Table 3. The adsorption capacity depends on various factors such as the physical and chemical properties of an adsorbent, the nature and initial concentration of the metal ion, the pH of the solution, and presence of other species. In view of this, a comparison of capacities of different adsorbents for a particular metal ion may not be appropriate. However, the adsorption capacity of composite chitosan biosorbent for copper is comparatively higher than most of the values shown in Table 3 and is less than those reported by Ni and Xu (6) on chitosan chelating resins, Juang et al. (8) on chitosan and Kondo et al. (10) on amidoxime chitosan resin. The biosorbent exhibits a higher adsorption capacity for nickel compared to chitosan and most of the cross-linked chitosans except that of EDTA- and DTPA-chitosans, as reported by Inoue et al. (9).

Column Adsorption

Dynamic column adsorption results for Cu (II) and Ni (II) on chitosan-coated alumina at 25°C and pH 4.0 are shown in Figs. 7 and 8, respectively. In the case of copper in the first cycle, no copper was found in the effluent up to 30 bed volumes and then the concentration of copper increases slowly. With respect to nickel, up to 45 bed volumes nickel was not present in the effluent and after that the concentration started to increase slowly. When the bed gets exhausted or when the effluent coming out of the column reaches the allowable maximum discharge level, the regeneration of the adsorption bed to recover the adsorbed

Table 3. Maximum capacity, Q^0 (mg/g) for adsorption of copper and nickel on various adsorbents

Adsorbent	Copper	Nickel	Reference
Anaerobically digested sludge	49.0	7.7	Gould & Genetelli (30)
Eutrophic peat	19.6		Chen et al. (31)
Treated G. *lucidum*	64.5		Rao et al. (32)
Amorphous iron hydroxide	14.0	6.8	Mustafa & Haq (33)
Sphagnum moss peat		9.2	Ho et al. (34)
Chitosan	16.8	2.4	Huang et al. (4)
Calcium-alginate	15.8	10.5	Huang et al. (4)
Activated slag	35.3	29.4	Gupta (28)
Chitosan acetate crown ethers	31.3	6.4	Tan et al. (13)
Cross-linked chitosan	80.0		Schmuhl et al. (15)
Grafted chitosan crown ether	41.3		Yang et al. (14)
Chitosan chelating resins	139.2		Ni & Xu (6)
Chitosan-sulfonic acid resin	94.1		Kondo et al. (2)
Chitosan	174.8		Juang et al. (8)
Amidoxime chitosan resin	153.2		Kondo et al. (10)
Metal imprinted chitosan	56.5	25.6	Tianwei et al. (16)
Ether cross-linking chitosan	82.4	52.9	Tianwei et al. (16)
EDTA-chitosan		123.3	Inoue et al. (9)
DTPA-chitosan		117.4	Inoue et al. (9)
Chitosan beads	80.7		Wan Ngah et al. (7)
Beads of chitosan cross-linked with glutaraldehyde, epichlorohydrin, and ethyleneglycol diglicidyl ether	59.6, 62.45, 45.9		Wan Ngah et al. (7)
Chitosan flakes	20.9		Bassi et al. (35)
Composite chitosan biosorbents	86.2	78.1	Present work

material becomes quite essential. The regeneration could be accomplished by a variety of techniques such as thermal desorption, steam washing, solvent extraction, etc. Each method has inherent advantages and limitations. In this study several solvents were tried to regenerate the adsorption bed. 0.1 M sodium hydroxide solution was found to be effective in desorbing and recovering Cu (II) and Ni (II) ions almost quantitatively from the adsorption bed. Maximum desorption of the metal takes place within 5 bed volumes and the complete regeneration could be achieved within 10 bed volumes. The bed was regenerated with 0.1 M sodium hydroxide solution when it was exhausted, and the same column was reused for subsequent adsorption experiments after washing it thoroughly with distilled water until the washings are pH neutral. The results of

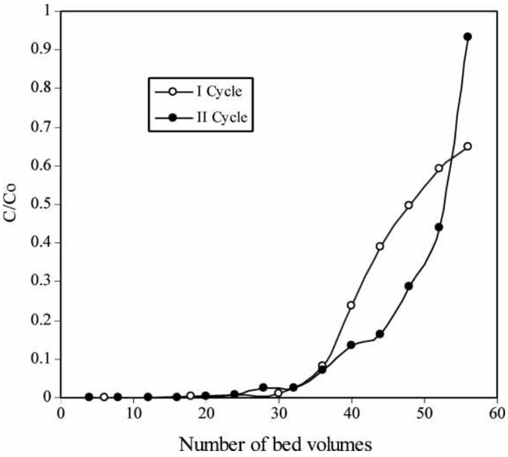

Figure 7. Experimental breakthrough curves for adsorption of Cu (II) on CCB, $C_0 = 105$ ppm, pH = 4.0, Flow rate = 2.0 ml/min, wt. of adsorbent = 17.96 g, Bed volume = 30 ml.

column adsorption on the regenerated bed are shown as II cycle in Figs. 7 and 8 for copper and nickel, respectively. In the II cycle, copper and nickel ions start appearing in the effluent at around 30 and 45 bed volumes, respectively. The results indicate that the decrease in the total adsorption capacity of composite chitosan biosorbent for copper and nickel is not significant.

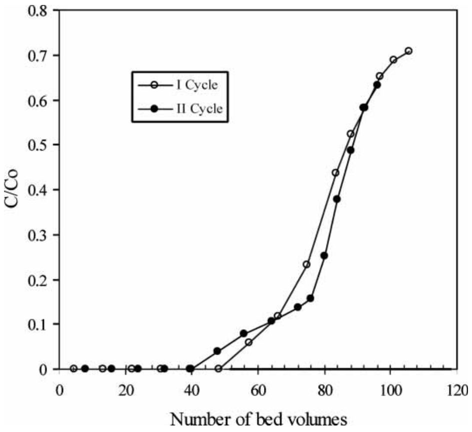

Figure 8. Experimental breakthrough curves for adsorption of Ni (II) on CCB, $C_0 = 103$ ppm, pH = 4.0, Flow rate = 2.2 ml/min, wt. of adsorbent = 17.87 g, Bed volume = 30 ml.

CONCLUSIONS

Composite chitosan biosorbent was prepared by coating chitosan on to ceramic alumina. The amount of chitosan present in the biosorbent was about 21%. The shape of the sorbent was nearly spherical with average particle diameter of about 100 ~ 150 μm. The equilibrium adsorption characteristics of the sorbent for Cu (II) and Ni (II) were studied. Based on the analysis of the FTIR spectra the binding mechanism for both Cu (II) and Ni (II) ions is essentially the same. The carboxylic and hydroxyl groups play a dominant role. The equilibrium sorption data were fitted to Langmuir, Freundlich, and Redlich-Peterson models and the model parameters were evaluated. The maximum monolayer capacities for Cu (II) and Ni (II), obtained from the Langmuir model, were compared with the literature results. In addition, column breakthrough studies were conducted. After the column became saturated with the metal ions, the column was regenerated with 0.1 M sodium hydroxide solution. The regenerated column was used for the second cycle, and it was found that there was no significant change in the adsorption capacity. The results of the limited number of adsorption-regeneration cycles indicated that the composite chitosan biosorbent could be used in water treatment. However, more adsorption-desorption studies need to be conducted at bench and pilot levels in order to implement a water treatment process based on CCB.

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