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Removal of Copper and Nickel from Aqueous Solutions Using Chitosan Coated on Perlite as Biosorbent

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Abstract: Chitosan has been increasingly studied as an adsorbent for removing heavy metal ions from aqueous solutions through adsorption due to the presence of free amino and hydroxyl groups. For most of the studies chitosan has been used in the form of flakes, powder, or hydrogel beads. Chitosan in its natural form has a tendency to agglomerate or to form gel in the aqueous medium. To overcome this problem a new composite chitosan biosorbent is prepared by coating chitosan, a glucosamine biopolymer on to perlite, a silicate ore. In the present investigation, equilibrium adsorption characteristics of Cu(II) and Ni(II) on newly developed biosorbent are studied. The effect of pH, agitation time, concentration of adsorbate, and amount of adsorbent on extent of adsorption are investigated. The experimental data are fitted to Langmuir and Freundlich adsorption isotherms, and to first-order Lagergren equation. The experimental results demonstrate that chitosan coated on perlite is an effective sorbent for immobilizing Cu(II) and Ni(II).

Keywords: Adsorption, chitosan, perlite, copper, nickel

INTRODUCTION

The fate of heavy metals in the environment has become an increasing concern. Process waste streams from mining operations, metal plating facilities, power generation facilities, electronic device manufacturing units, and tanneries often contain heavy metal ions like mercury, chromium, cadmium,

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lead, nickel, and copper at concentrations above local discharge limits. Precipitation, oxidation and reduction, ion exchange, filtration, reverse osmosis, electro-chemical removal, and evaporative recovery can all potentially be used to treat industrial effluents for metals. These methods are inefficient for heavy metal contaminant at tracer amounts in larger volume of solution. To meet environmental regulations, these industrial effluents contaminated with heavy metals must be treated before discharge. Studies on treatment of effluents bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among the physicochemical treatment processes. Activated carbons are the most widely used adsorbents because they have an excellent adsorption capacity for metal removal, but their use is usually limited due to the high cost. This has led many workers to search for cheap or more effective constituents such as bagasses and flyash (1), cork biomass (2), Sawdust (3), Chitin and chitosan (4, 5).

Chitosan is obtained by deacetylation of chitin, which is extracted from shrimp, crab, some fungi (6), and other crustaceans. Chitosan is not only inexpensive and abundant in nature, but also a good adsorbent for heavy metals. Chitosan chelates five to six times greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin (7). 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 (8). To overcome some of the problems associated with the use of pure chitosan, 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 chitosan coated on perlite beads are characterized before and after adsorption of Cu(II) and Ni(II) by FTIR spectroscopy. Further, the study is extended to investigate the effect of pH, time, adsorbate concentration, and adsorbent dosage on extent of adsorption of Cu(II) and Ni(II) on chitosan coated perlite.

EXPERIMENTAL

The expanded form of perlite is obtained from Silbrico Corporations, IL. Chitosan, copper sulphate, and nickel ammonium sulphate are procured from Aldrich Chemical Corporation. Oxalic acid and sodium hydroxide are purchased from Fisher Scientific Company. A stock solution containing 1000 ppm of Cu(II) and Ni(II) are prepared in double distilled water. All the working solutions are obtained by diluting the stock solution with double distilled water.

Preparation of Chitosan Coated Perlite Beads

Perlite, which is composed mainly of alumina and silica, is used as a substrate for the preparation of beads (9). Perlite is first mixed using 0.2 M oxalic acid and the mixture is stirred for 12 h at room temperature and filtered. The filtered perlite is washed with deionized water and dried overnight at 70°C, and sieved through 100-mesh size. The acid-treated perlite is stored in desiccator. About 30 g of medium molecular weight chitosan is slowly added to 1L of 0.2 M oxalic acid solution under continuous stirring at 40–50°C to facilitate the formation of viscous gel. About 60 g of acid-treated perlite powder is mixed with demonized water and slowly added to the diluted gel and stirred for 12h at 40–50°C. The highly porous beads are then prepared by drop-wise addition of perlite gel mixture into a 0.7 M NaOH precipitation bath (10). 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 demonized water to a neutral pH. The beads were dried in a freeze drier, oven, and by air.

Adsorption Experiments

In order to explore the effect of influencing factors, such as pH, contact time, quantity of adsorbent, and the initial concentrations of metal solution, a series of batch experiments are conducted. The stock solution is diluted to required concentrations (50, 100, 150, and 200 ppm). Batch adsorption experiments are performed by agitating specified amount of adsorbent in 100 mL of metal solutions of desired concentrations at varying pH in 100 mL stopper bottles. The pH of the suspension in experiments is adjusted with 0.01 N HCl and 0.01 N NaOH. The reaction mixture is agitated at 200 rpm for a known period of time at room temperature in a mechanical shaker. After equilibrium, the aqueous-phase concentration of metal is analyzed with atomic absorption spectrophotometer (Perkin–Elmer 2380). Adsorption of metal on the glassware is found to be negligible and is determined by running blank experiments. Each experiment is repeated at least three times and mean values are taken. The absolute deviation was found to be 3%. The amount adsorbed per unit mass of adsorbent at equilibrium q_e (mg/g) is obtained using the equation.

$$q_e = \left(\frac{C_i - C_e}{m}\right) \cdot v \tag{1}$$

where C_i and C_e denote the initial and equilibrium metal concentrations (ppm), respectively. v is the volume of the solution, and m is the mass of the adsorbent used (g). Infrared spectrums of chitosan coated perlite before and after adsorption of metal ions are measured in the frequency range of 400–4000 cm^{-1}. The samples are formed into pellets with KBr and the spectra are recorded on a Bomen FTIR, MB-series.

RESULTS AND DISCUSSION

High-temperature pyrolysis experiments are conducted at 800°C to determine the amount of chitosan coated over perlite. Two ceramic crucibles, one containing acid washed pure perlite and the other one containing chitosan-coated perlite, are placed inside a furnace heated at 800°C. The chitosan burn out at this temperature and the chitosan content are determined from weight difference. The results indicated that 23% of chitosan is coated on perlite. Perlite does not have any particular shape or crystalline structure and it appears more like flakes.

FTIR absorption spectra before and after Cu(II) and Ni(II) sorption are shown in Figs. 1, 2, and 3, respectively. The characteristic structure of the FTIR spectra of untreated chitosan coated on perlite (Fig. 1) shows peaks at 1641 cm^{-1}, 3360 cm^{-1}, and 1300 cm^{-1} due to the presence of amino, hydroxyl, and ether groups, respectively. The peaks at these wave numbers, which are intact, indicate that the functional groups are not disturbed due to the coating process. The presence of unprotonated amino groups in the bead serves as an active binding site for metals. The degree of adsorption of metal ions on chitosan is a distinguishable feature, which can be followed through infrared spectroscopy. Figures 2 and 3 indicate that there is a shift

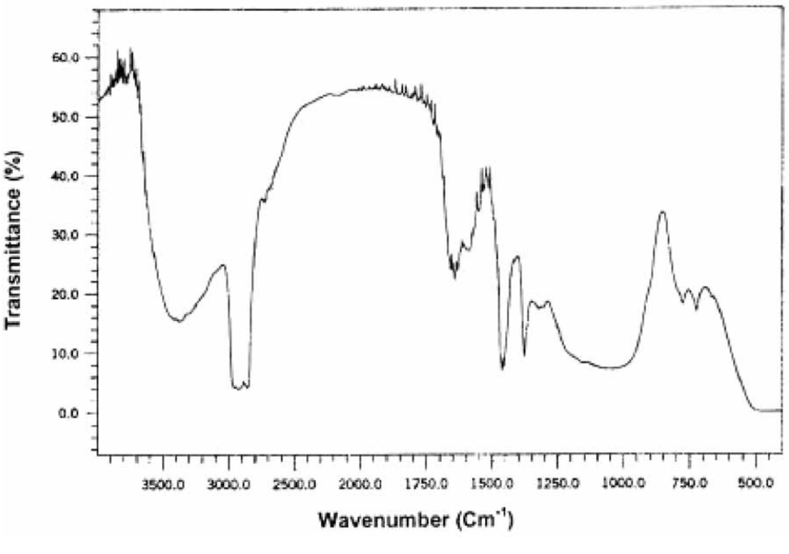

Figure 1. FTIR spectrum of chitosan-coated perlite beads.

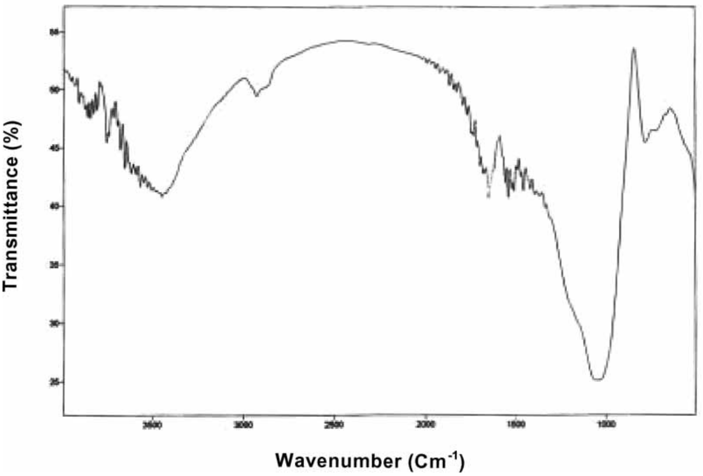

Figure 2. FTIR spectrum of adsorption of Cu(II) on chitosan-coated perlite beads.

in absorption frequency of amino and hydroxyl groups indicating the deformation of O–H and N–H bands. This may be attributed to interaction between the functional groups and metal ions as a result of adsorption.

Transport studies conducted by Findon et al. (11) suggested that copper is chelated with the NH_2 and OH groups in the chitosan chain. The study of Chui et al. (12) confirms that the amino groups of chitosan are the major effective binding sites for metal ions, forming stable complexes by coordination. The nitrogen electrons present in the amino groups can establish dative bonds

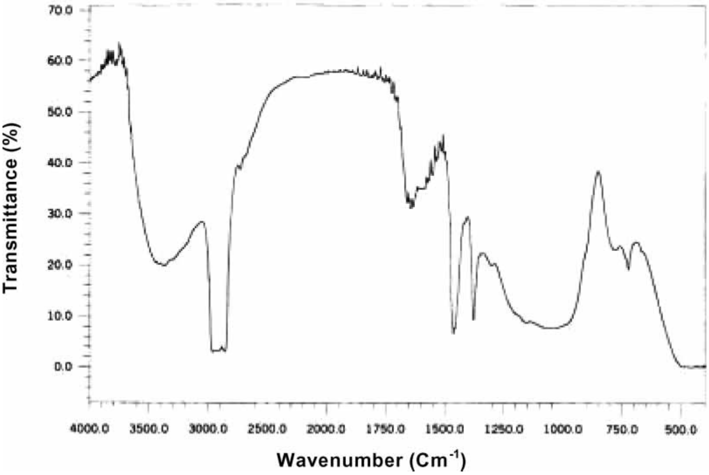

Figure 3. FTIR spectrum of adsorption of Ni(II) on chitosan-coated perlite beads.

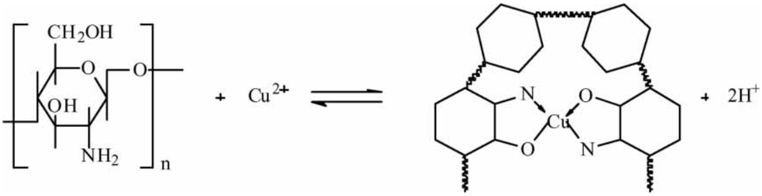

Figure 4. Formation of complexation between chitosan and copper ion.

with transitional metal ions. Some hydroxyl groups in these biopolymers may function as donors. Hence deprotonated hydroxyl groups can be involved in the coordination with metal ions (13). Inoue et al. (14) suggested that chitosan forms chelate with metal ions by releasing hydrogen ions. Formation of a complex between chitosan and copper ions is shown in Fig. 4.

Sorption Kinetics

Sorption kinetics is important physicochemical parameters to evaluate the basic qualities of a good sorbent (such as whether or not the sorbent adsorbs metals). Removal of Cu(II) and Ni(II) by chitosan as a function of time at pH 5.0, at various initial concentrations (50–200 ppm), is shown in Figs. 5 and 6. The results indicate that the adsorption capacity of Cu(II) and Ni(II) ions increased monotonically to saturation with time, and maximum adsorption is attained at 120 min for Cu(II) and at 180 min for Ni(II),

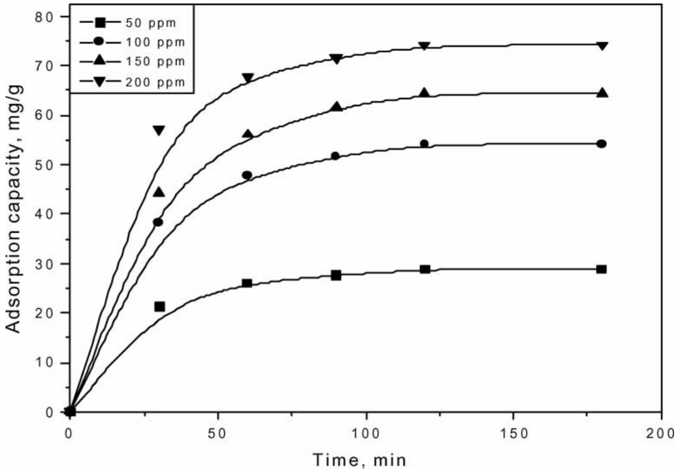

Figure 5. Effect of agitation time and initial concentration on adsorption of Cu(II) on chitosan-coated perlite beads.

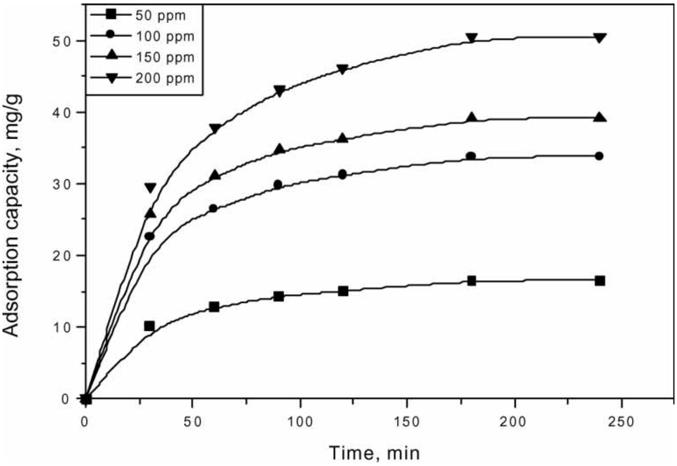

Figure 6. Effect of agitation time and initial concentration on adsorption of Ni(II) on chitosan-coated perlite beads.

respectively. Therefore, these times are sufficient to attain equilibrium for Cu(II) and Ni(II) ions on chitosan coated on perlite. The kinetics of Cu(II) and Ni(II) adsorption on chitosan coated on perlite are determined using Lagergren's equation.

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

where q_e is the amount of sorbate adsorbed per unit weight of sorbent at equilibrium (mg/g), q_t is the amount of sorbate uptake per unit weight of sorbent at any time t (mg/g), t is the time in minutes, and K_{ad} is the rate constant of adsorption. The values of K_{ad} are calculated from the slopes of the plot of log $(q_e - q_t)$ vs. t for different concentrations and the values of these constants are given in Table 1. There is no significant change in the values of K_{ad} at various concentrations of Cu(II) and Ni(II).

Effect of pH

In order to optimize the pH for maximum removal efficiency, experiments are conducted with 100 mL of 100 ppm of metal solution containing 0.1 g of chitosan coated on perlite in the pH range 3 to 5 for copper and 3 to 8 for nickel at room temperature. This pH range is chosen because below pH 2 chitosan undergoes dissolution and copper and nickel ions get precipitated above pH 5 and 8, respectively. The results are depicted in Fig. 7. From the figure it is clear that the removal of Cu(II) and Ni(II) is maximum at pH 5 and decreases at lower and higher pH values. Low pH would favor protonation

Table 1. Adsorption rate constants of lagergren plot for Cu(II) and Ni(II) on chitosan-coated perlite beads

	Metal ions			
	Cu(II)		Ni(II)	
Initial concentrations of metal ion solutions (ppm)	K_{ad}	R^2	K_{ad}	R^2
50	0.029	0.9967	0.0161	0.9964
100	0.030	0.9997	0.0165	0.9959
150	0.031	0.9976	0.0170	0.9951
200	0.032	1	0.0172	0.9999

of the amino sites, resulting in a reversal of charge, and would greatly diminish the metal chelating ability of chitosan. At low pH value, the H^+ ions compete with metal cations for the exchange sites in the system there by partially releasing the latter. The heavy metal cations are completely released under extreme acidic conditions (15–17).

Effect of Adsorbent Dose

The dependence of adsorption of Cu(II) and Ni(II) on the amount of chitosan-coated perlite is studied at room temperature and at pH 5.0 by varying the adsorbent doses from 0.05 g to 0.3 g, while keeping the volume and concentrations of the metal solution constant. The results are graphically shown in

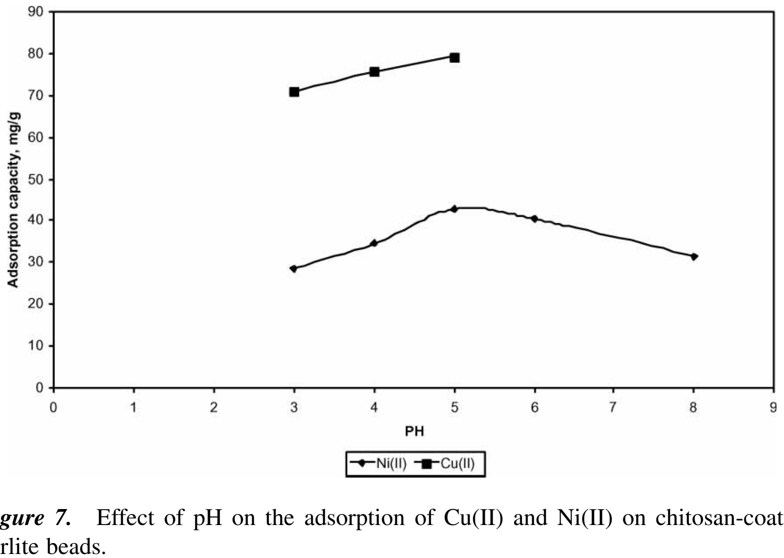

Figure 7. Effect of pH on the adsorption of Cu(II) and Ni(II) on chitosan-coated perlite beads.

Fig. 8. It is apparent that the percent removal of Cu(II) and Ni(II) increases rapidly with increase in the dose of adsorbent due to the greater availability of the adsorbent. Adsorption is maximum with 0.3 g of chitosan-coated perlite and the maximum percentage removal is about 97% and 95% with chitosan-coated perlite for Cu(II) and NI(II), respectively.

Equilibrium Modeling

Modeling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures (18). To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data at pH 5.0 and room temperature, initial metal concentrations are varied while the biomass weight in each sample is kept constant. Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing finite number of adsorption sites of uniform energies of adsorption with no transmigrates of adsorbate in the plane of the surface. The experimental data are fitted to Langmuir isotherm,

$$q_e = \frac{Q^o b C_e}{(1 + bC_e)} \tag{3}$$

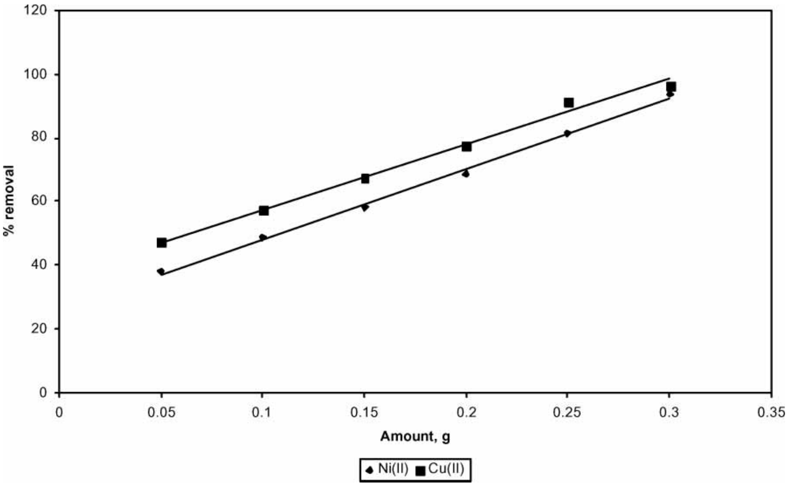

Figure 8. Effect of dose of adsorbent on the percent removal of Cu(II) and Ni(II) on chitosan-coated perlite beads.

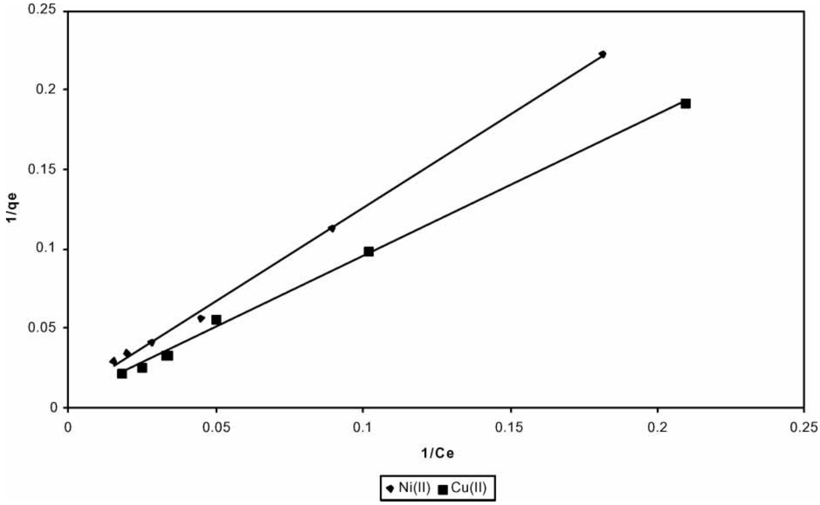

Figure 9. Langmuir isotherm for adsorption of Cu(II) and Ni(II) on chitosan-coated perlite beads.

where q_e is the amount of metal adsorbed (mg/g), C_e is the equilibrium concentration of solution in (ppm), Q° and b are Langmuir constants released to adsorption capacity and energy of adsorption respectively. The adsorption isotherm is shown in Fig. 9. The values of Q° and b obtained form these plots are listed in Table 2. To lesser extent, the equilibrium data are also well described with the Freundlich equation, probably due to the real heterogeneous nature of the surface sites involved in the metal uptake (19).

The Freundlich equation is of the form,

$$\log q_e = \log K_F + \frac{1}{n \log C_e} \tag{4}$$

where K_F and n are Freundlich constants. Experimental data of the present study are fitted to Eq. (4) and the parameters (K_F and n) are evaluated from the plot of log q_e vs. log C_e (Fig. 10). The Freundlich parameters K_F and n

Table 2. Parameters of Langmuir and Freundlich isotherms for adsorption of Cu(II) and Ni(II) on chitosan-coated perlite beads

	Langmuir constants			Freundlich constants		
Metal ions	Q^o	b	R^2	K_f	n	R^2
Cu (II)	196.08	0.0057	0.9992	1.276	1.098	0.9948
Ni (II)	114.95	0.0075	0.9988	1.181	1.207	0.9882

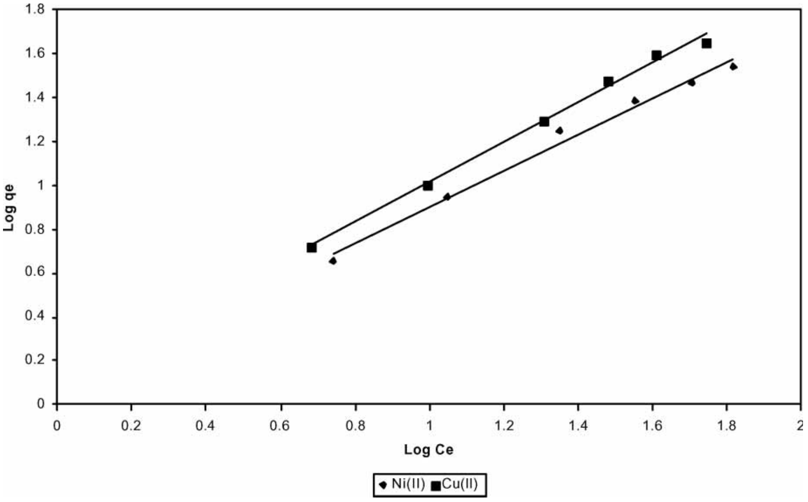

Figure 10. Freundlich isotherm for adsorption of Cu(II) and Ni(II) on chitosan-coated perlite beads.

with the correlation coefficients R^2 are also presented in Table 2. More generally, the application of the Langmuir model seemed to be more appropriate than the Freundlich model. A comparison of adsorption capacity of chitosan or other chemically modified chitosan adsorbents are presented in Table 3. The adsorption capacity of the new material is considerably greater than the other chitosan-based adsorbents.

CONCLUSIONS

Chitosan is effectively coated on an inert substrate, perlite, and is made in the form of spherical beads. Pyrolysis results indicated that 23% of chitosan was coated on perlite. In this study adsorption of Cu(II) and Ni(II) on chitosan-coated perlite has been investigated. The data obtained through this work supports that the chitosan-coated perlite is an effective low-cost adsorbent for the removal of Cu(II) and Ni(II) in aqueous solution. The adsorption of metal ions is heavily dependent on the amount of adsorbent, concentration of metal ions, agitation time, and pH of the metal solution. Maximum removal of Cu(II) and Ni(II) on chitosan coated on perlite is at pH 5.0. The equilibrium adsorption data are correlated by Langmuir and Freundlich isotherm equations. The maximum monolayer adsorption capacity of chitosan coated on perlite is 196.07 mg/g for Cu(II) and 114.94 mg/g for Ni(II), respectively. Rate constants for adsorption are calculated from the Lagergren's equation. The equilibrium adsorption data showed that chitosan

Table 3. Maximum capacity (mg/g) for adsorption of Cu(II) and Ni(II) on various adsorbents

	Maximum adsorption capacity (mg/g)			
Adsorbent	Cu(II)	Ni(II)	pH	Reference
EDTA–Chitosan	—	123.3	2.0	20
DTPA–Chitosan	—	117.4	2.0	20
Chitosan	137.0	—	4.0	21
	59.0	—	5.0	11
	56.3	—	5.0	22
	80.0	—	3.5	4
	71.2	—	4.5	4
	16.8	2.4	5.0	23
Non-cross-linked chitosan	80	—	5.0	24
Chitosan acetate crown ether (CCTS–1)	23.9	0.7	5.6	25
Chitosan diacetate crown ether (CCTS–2)	31.3	4.1	5.6	25
Epichlorohydrine cross-linked chitosan (CCTS)	16.8	6.4	5.6	25
Chitosan-coated perlite	196.07	114.94	5.0	Present study

coated beads adsorbed significant amount of Cu(II) and Ni(II) compared to chitosan or other chemically modified chitosan as reported in the literature.

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