

Dispersion of chitosan on perlite for enhancement of copper(II) adsorption capacity

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Abstract

Chitosan coated perlite beads were prepared by drop-wise addition of slurry, made of chitosan dissolved in oxalic acid and perlite, to an alkaline bath (0.7 M NaOH). The beads that contained 32% chitosan enhanced the accessibility of OH and amine groups present in chitosan for adsorption of copper ions. The experiments using Cu(II) ions were carried out in the concentration range of 50–4100 mg/L (0.78–64.1 mmol/L). Adsorption capacity for Cu(II) was pH dependent and a maximum uptake of 104 mg/g of beads (325 mg/g of chitosan) was obtained at pH 4.5 when its equilibrium concentration in the solution was 812.5 mg/L at 298 K. The XPS and TEM data suggested that copper was mainly adsorbed as Cu(II) and was attached to amine groups. The adsorption data could be fitted to one-site Langmuir adsorption model. Anions in the solution had minimal effect on Cu(II) adsorption by chitosan coated perlite beads. EDTA was used effectively for the regeneration of the bed. The diffusion coefficient of Cu(II) onto chitosan coated beads was calculated from the breakthrough curve and was found to be $2.02 \times 10^{-8} \text{ cm}^2/\text{s}$.

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1. Introduction

Copper containing waste streams are generated from a variety of industries including metal finishing, copper electroplating, and cooling water systems. The concentration of copper in these streams can be in the range of 20–2200 mg/L. The maximum contaminant level goal for copper, as suggested by the US EPA, is 1.3 mg/L. Therefore, copper concentration of any industrial effluents should be reduced below 1.3 mg/L before discharging to the environment. Although copper can exist as Cu(0), Cu(I), and Cu(II), the main species of concern in aqueous solution is Cu(II) [1]. Cu(II) binds easily to organic and inorganic matter in aqueous solution based on solution pH [2]. These Cu(II) species pose a significant threat to aquatic life and render natural water unsuitable for the public use.

A number of methods including precipitation and adsorption have been employed for the removal of copper from industrial

effluents. Precipitation is the most frequently used method. An adsorption process can be an attractive alternative method for Cu(II) removal, if a low cost adsorbent that can be regenerated for repeated use is available. In recent years, bioadsorbents are found to be promising adsorbents for removal of metal ions because of their chelating ability. Materials such as *Sphagnum* moss peat, *Rhizopus arrhizus*, *Mucor miehei*, biopolymers, algal biomass [3–7] have been tried for removal of varieties of heavy metal ions including chromium, cadmium, copper, and uranium. In fungal biomasses, metal ion sorption mainly occurs in the cell wall, which consists of a network of amino-polymers and glucans [8]. The ability of chitosan to bind with transition metals makes it an attractive adsorbent for copper [9].

Chitosan, which is obtained by deacetylation of chitin, is readily soluble in organic acids and is easily fabricated into beads, gels, and films. The main parameters that influence physical and chemical properties of chitosan are its molecular weight and degree of acetylation [10]. Generally, hydroxyl (OH) and amine (NH₂) groups in chitosan are available for characteristic coordination bonding with metallic ions such as Cu(II), Cd(II), Cr(III), Cr(VI), and U(VI) [11–13].

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Several researchers [14–19] have investigated chitosan as an adsorbent for removal of heavy metals from aqueous streams. Chitosan is a natural biopolymer, hydrophilic, and has the ability to form complexes with metals. It is also a non-toxic, biodegradable and biocompatible material. According to Rorrer et al. [16] chitosan flake or powder swells and crumbles making it unsuitable for use in an adsorption column. Chitosan also has a tendency to agglomerate or form a gel in aqueous media. Although the amine and hydroxyl groups in chitosan are mainly responsible for adsorption of metal ions, these active binding sites are not readily available for sorption when it is in a gel or in its natural form [17]. Guibal et al. [18] noted that the maximum uptake of chitosan flakes was about half of that obtained with chitosan beads for molybdate. The adsorption capacity can be enhanced by spreading chitosan on physical supports that can increase the accessibility of the metal binding sites. Boddu et al. [20] coated alumina with chitosan and investigated the adsorption capacity for chromium. They observed that chitosan beads produced with high internal surface area boosted the metal binding capacity. Several attempts have been made to chemically modify the structure of chitosan, and its performance has been evaluated through adsorption of heavy metal ions from aqueous solutions. The amine and hydroxyl groups in chitosan allow a variety of chemical modifications [21].

Kawamura et al. [22] prepared a porous polyaminated chitosan chelating resin by cross-linking poly(ethylene amine) onto chitosan beads. The resultant beads showed high capacity and high selectivity for the adsorption of metal ions. Chang and Chen [23] investigated the adsorption of copper on magnetic nano-chitosan beads. They found that the chitosan-bound Fe_3O_4 nanoparticles were efficient for the removal of Cu(II) ions at $\text{pH} > 2$ with a maximum adsorption capacity of 21.5 mg/g. A number of attempts have been made to enhance the acid resis-

tance of chitosan through cross-linking with various chemicals [24–28], however, the sorption capacity for metal ions generally decreased.

Li and Bai [29] investigated a new amine shielding method for cross-linking chitosan with ethylene glycol diglycidyl ether (EGDE) to improve the chemical stability of beads in acidic conditions. They treated chitosan hydrogel beads with formaldehyde before cross-linking with EGDE, which made the beads acid resistance and increased adsorption capacity significantly. Hasan et al. [17] noted that by dispersing chitosan on an inert substrate, perlite, its adsorption capacity for Cr(VI) could be enhanced. Kalyani et al. [30] used chitosan coated perlite beads to adsorb copper and nickel from aqueous solution. It is assumed that the active group, such as NH_2 became more readily available when chitosan is dispersed on perlite.

Perlite is a naturally occurring dense glassy volcanic rock which consists mainly of fused sodium potassium aluminum silicate (greater than 70%) and 3–5% water. When it is heated at temperatures in the range of 850–1100 °C, it expands 4–35 times of its original volume and is called ‘expanded perlite’. The expanded perlite is white in color, and has a density of 32 kg/m³ (2 lb/ft³). Perlite is generally chemically inert and has a pH of approximately 7. However, silanol groups can form on the perlite surface providing various adsorption properties. The surface characteristics of perlite can also be modified to some extent by varying the pH of the solution.

Kalyani et al. [30] did not provide a detailed analysis of the adsorption mechanism, particularly the role of perlite. The maximum adsorption capacity was determined from the extrapolation of the Langmuir equation rather than from the experimental data. This approach can lead to overestimation if the experimental data are not obtained up to the saturation capacity. The adsorption capacity of copper by various adsorbents is summarized in Table 1.

Table 1
Maximum adsorption capacity of various adsorbents for copper

Adsorbent	pH	Adsorption capacity (mg/g)	Maximum initial concentration (mg/L)	References
Imprinted chitosan resin	5.0	174	324	[31]
Chitosan (shrimp)	5.5	152.7	325	[32]
Chitosan (crab)	5.5	168.2	325	[32]
Chitosan (lobstar)	5.5	165.2	325	[32]
Chitosan (cuttlebone)	5.5	235.9	325	[32]
Chitosan	5.0	160	288	[33]
Chitosan (shrimp)	5.0	300	123.1	[34]
Chitosan	5.0	80	1000	[35]
Crab shell	5.0	62.7	112	[14]
Ni^{2+} imprinted chitosan	5.5	56.5	100	[36]
Chitosan	5.6	93.4	1600	[37]
Chitosan based resin	5.6	131.2	1600	[37]
Chitosan	6.0	20	20	[13]
Activated carbon (coal)	5.0	4.5	6.4	[43]
Activated carbon (coconut shell)	5.0	7.04	6.4	[43]
Cellulose adsorbent	5.0	63.5	381	[25]
Amidoxime chitosan resin	5.0	93.4	32	[38]
Chitosan coated perlite	5.0	196	>1000	[30]
Chitosan coated perlite bead	4.5	104	1000	Present work
Chitosan (perlite free basis)	4.5	325	1000	Present work

In this work, chitosan was coated/dispersed on perlite to enhance the accessibility of OH and amine groups for adsorption of copper ions. The adsorbent of chitosan coated onto perlite was prepared as spherical beads and was evaluated for removal of Cu(II) in the concentration range of 50–4100 mg/L (0.78–64.1 mmol/L). Both the isotherm data and dynamic breakthrough curves were obtained to gain a better understanding of the adsorption process. The mechanism for copper adsorption on chitosan was explored, and the regeneration of chitosan beads using ethylene diamine tetraacetic acid (EDTA) for repeated use was studied.

2. Materials and methods

2.1. Materials

Perlite, grade YM 27, was obtained from Silbrico Corporation, IL, USA. Composition and various properties of perlite are given in the website (www.silbrico.com). Chitosan and copper sulfate were procured from Aldrich Chemical Corporation, WI, USA. The chitosan used in this study was 75–85% deacetylated and had a molecular weight of ~190,000–310,000 as reported by Aldrich Chemical Corporation. All chemicals used in this study were of analytical grade. Oxalic acid, EDTA and sodium hydroxide were purchased from Fisher Scientific, NJ, USA. A stock solution containing 5000 mg/L of Cu(II) was prepared in distilled, deionized water using copper sulfate. The working solutions of various Cu(II) concentrations were obtained by diluting the stock solution with distilled water.

2.2. Preparation of chitosan coated perlite beads

Perlite powder of 35 mesh was first soaked with 0.2 M oxalic acid for 4 h to remove any acid soluble constituents of perlite and also to introduce acidic groups onto perlite surface that may enhance the adherence of chitosan to perlite. Acid treated perlite was washed with distilled water and dried in an oven for 12 h. This was done to maintain a proper ratio of acid to chitosan in the mixture during bead making process. Thirty grams of chitosan flakes was dissolved in 1 L of 0.2 mol/L oxalic acid solution to prepare a gel. To this gel, 60 g of perlite treated with oxalic acid is added. The mixture was stirred for 4 h while heating at 313–323 K (40–50 °C) to obtain a homogeneous mixture. The spherical beads of chitosan coated perlite were prepared by drop-wise addition of the mixture into a 0.7 M NaOH precipitation bath. The beads were washed with deionized water to a neutral pH and freeze dried for the subsequent use. Pure chitosan beads were prepared in a similar manner. Chitosan was dissolved in oxalic acid and the resulting gel was added drop wise to the NaOH precipitation bath.

2.3. Experimental procedure

Equilibrium batch adsorption studies were carried out by exposing 0.25 g of beads to 100 mL solutions containing Cu(II) ions at different concentrations in 125 mL Erlenmeyer flasks

at a pre-determined temperature. The initial concentration of the Cu(II) ions in the solution ranged from 50 to 4100 mg/L (0.78–64.1 mmol/L). While studying the effect of pH on the adsorption capacity, the initial pH of the solutions was adjusted to a desired value by adding either 0.1 M sulfuric acid or 0.1 M sodium hydroxide solution. The pH of the solution in each flask was not controlled during adsorption process. The flasks were placed in a shaker bath at a desired temperature and were agitated at 200 rpm for various periods of time. It was found from the analysis of samples at various time intervals that 24 h was sufficient to attain the equilibrium. During kinetic study, samples were taken from each flask at different time intervals for the first 2 h of exposure, and the concentration of copper in the solution was analyzed by atomic absorption spectroscopy. The adsorption isotherm was obtained by varying the initial concentration of Cu(II) ions in the solution. The amount of Cu(II) adsorbed per unit mass of adsorbent (q_e) was calculated using the following equation.

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

where C_i and C_e represent initial and equilibrium concentrations in milligram per liter, respectively. V is the volume of the solution in liter (L) and M is the mass of the adsorbent in gram.

3. Results and discussion

3.1. Characterization of beads

The chitosan content of coated perlite beads was determined using a thermogravimetric analyzer (TGA). The sample was heated to 800 °C at a rate of 10 °C per minute. Chitosan started to decompose at 200 °C and burnt out completely at 500 °C. It was found that about 32% of chitosan was coated on perlite. The physical properties of the pure chitosan beads and chitosan coated perlite beads are given in Table 2. The pore size distribution of chitosan flake, pure chitosan beads, and chitosan coated perlite beads is shown in Fig. 1. The average pore diameter of chitosan coated perlite beads was found to be 0.0068 μm, whereas the average pore diameter of chitosan flake and pure chitosan beads were 0.004 and 0.0047 μm, respectively. The average pore volume of chitosan flake, pure chitosan beads,

Table 2
Physical properties of chitosan coated perlite beads

Parameter	Chitosan coated perlite bead	Pure chitosan bead
Average particle diameter, d_p (m)	2.2×10^{-3}	2.2×10^{-3}
Particle density, ρ_p (kg/m ³)	272	800
Particle porosity, ϵ_p	2.56×10^{-3}	–
Physical nature	Porous	–
Shape of the bead	Spherical	Spherical
Chitosan content (wt%)	32	100
Surface area (m ² /g)	4.5	2.99
Pore volume (cm ³ /g)	9.4×10^{-3}	1×10^{-3}
Pore radius (m)	4.13×10^{-9}	2.86×10^{-9}
Bed void fraction, ϵ	0.498	–

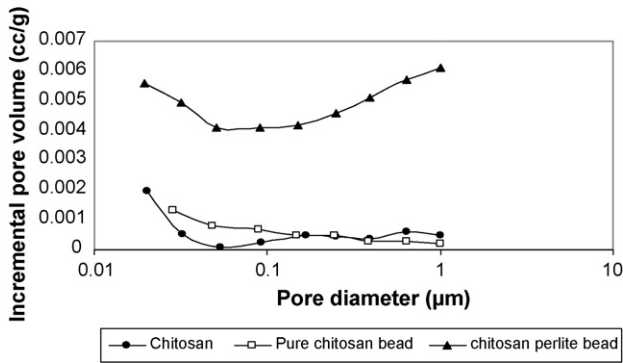


Fig. 1. Pore size and pore volume distribution of chitosan, pure chitosan beads, and chitosan coated perlite beads.

and chitosan coated perlite beads was found to be 1×10^{-3} , 1.01×10^{-3} , and $9.41 \times 10^{-3} \text{ cm}^3/\text{g}$, respectively. As can be seen from SEM micrographs of the cross-section of the bead (Fig. 2), it was rather porous in nature compared to pure chitosan beads. The increase in pore volume of chitosan coated perlite beads suggests that more intra-particle space than pores within perlite particles. Chitosan film held these particles together and in the process was dispersed on perlite.

3.2. Influence of coating chitosan onto perlite powder

The batch adsorption data for adsorption of copper on chitosan flake, pure chitosan beads and chitosan dispersed perlite beads were obtained to study the enhancement of copper adsorption by chitosan due to dispersion on perlite (see Fig. 3). Chitosan coated perlite beads exhibited highest capacity for copper on per gram of chitosan basis. Interestingly, chitosan flakes had a higher capacity for Cu(II) than pure chitosan beads although they had almost a similar pore diameter and pore volume. This may be due to the reduction of surface area when pure chitosan beds were formed. It may be noted that pure chitosan beads were essentially non-porous. It appears that the coating of chitosan on an inert surface enhanced the overall adsorption capacity. Perlite particles are found to have negligible capacity for Cu(II). Also TEM micrograph (Fig. 4) of chitosan beads that were exposed to copper showed that copper (grey spot) was present mainly in the vicinity of chitosan film.

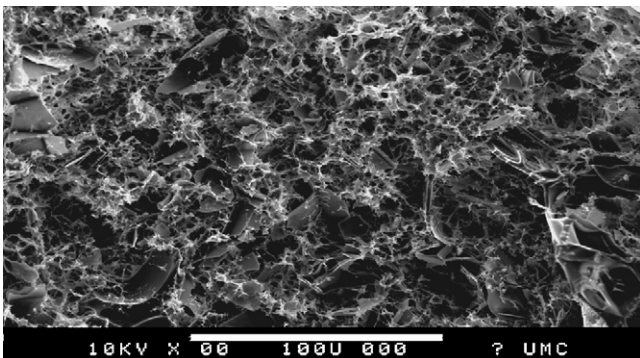


Fig. 2. Scanning electron micrograph of chitosan coated perlite beads.

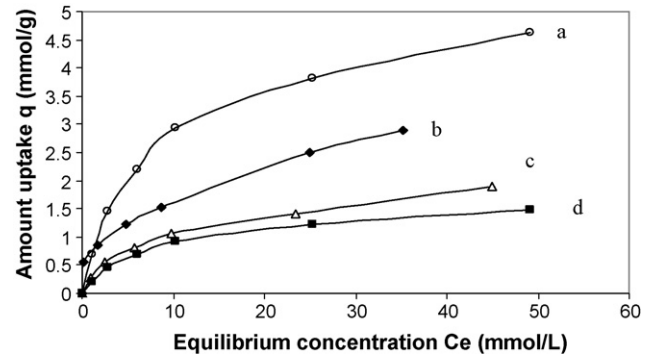


Fig. 3. Equilibrium uptake of Cu(II) onto (a) chitosan coated perlite beads when expressed as perlite free basis, (b) chitosan flake, (c) pure chitosan beads, and (d) chitosan coated perlite beads.

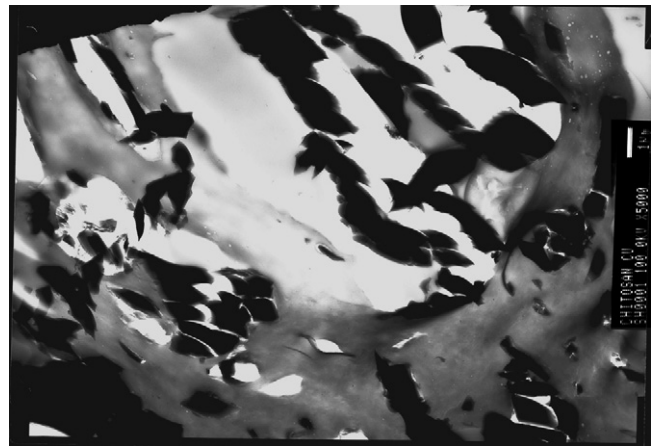


Fig. 4. Transmission electron micrograph of chitosan coated perlite beads exposed to CuSO_4 (black spots, perlite; white spots, chitosan film; grey spots, Cu).

3.3. Effect of pH on copper uptake by chitosan coated perlite beads

The uptake of Cu(II) at different pH of the solution is shown in Fig. 5. The pH of the solution affects the degree of ionization, the surface charge, and the speciation of copper, all of which can impact the adsorption mechanism and the uptake capacity. The pH of the solution was found to increase at the end of

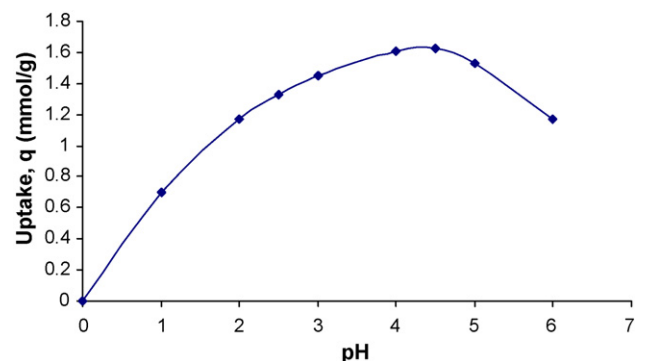


Fig. 5. Effect of pH on Cu(II) removal by chitosan coated perlite beads (concentration of copper: 1.563 mmol/L , amount of beads: $0.25 \text{ g}/100 \text{ mL}$).

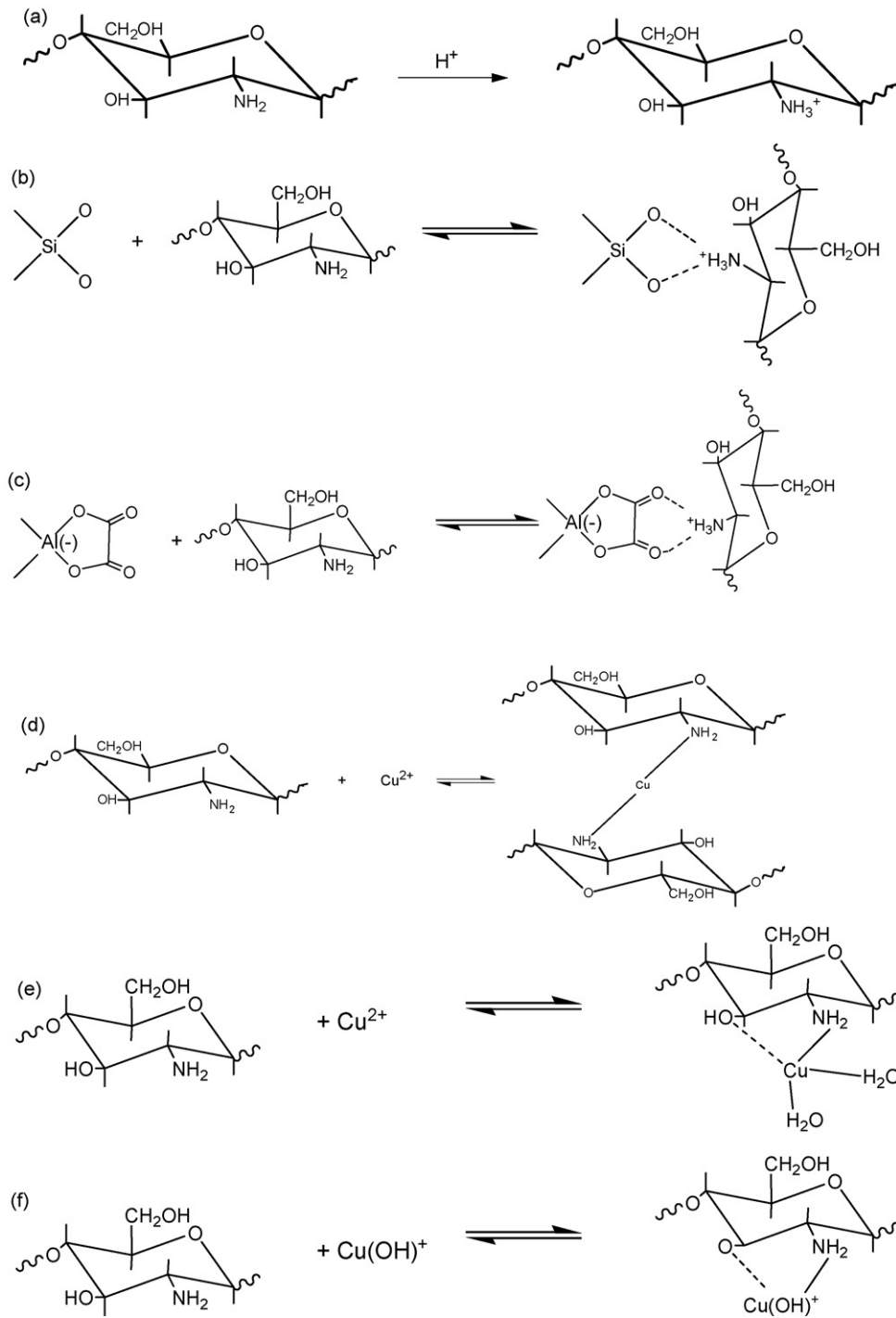


Fig. 6. Possible reaction mechanisms for copper uptake by chitosan coated perlite beads.

an adsorption run, and no attempt was made to maintain a constant pH during the course of the experiment using a buffer solution. This was done to understand the effect of pH under normal industrial operating conditions in a column where it is not expected to maintain a constant pH. The adsorption of copper ions should result in a release of H^+ ion. This should normally reduce the pH of the solution. However, Kaminski and Modrzejewska [39] noted that the exchange of released H^+ ions occurs between the surface of the bead and solution resulting in the increase of pH of the solution. The increase in pH can also

be attributed to the protonation of amine groups in chitosan according to the reaction shown in Fig. 6(a). Depending on the solution pH, amine groups can undergo protonation to either NH_3^+ or $(\text{NH}_2\text{-H}_3\text{O})^+$. The extent of protonation depends on the solution pH. According to Udaybaskar et al. [42], the extent of protonation of chitosan can be as high as 99% at a pH of 4.3. However, it decreases as the pH is increased. The extent of protonation is 91, 50, and 9% at pH 5.3, 6.3, and 7.3, respectively. As explained later, mainly NH_2 groups participated in binding with copper. Since the maximum adsorption of copper was

noted at a pH of 4.5, it appears that the presence of perlite in the beads slowed down the protonation of chitosan around this pH and prevented formation of NH_3^+ groups (Fig. 6(b and c)). The surface charge analysis of the bead provided further information regarding the adsorption mechanism and is discussed below.

In our study, the increase in pH of the final solution could be attributed to both the mechanism; surface exchange and protonation. The uptake of Cu(II) by chitosan beads increased as pH increased from 1 to 4.5. It then started to decrease as the pH was further increased. At pH of 7.0, Cu(II) started to precipitate out from the solution. Verbych et al. [19] also reported an increase in copper adsorption on chitosan with the increase of solution pH in the range of 1–5, having a maximum capacity within the pH range of 4–5.

The surface charge on the bead is also dependent on pH and provided a better understanding of the type of bond formed between Cu(II) and the surface. The surface charge of the beads were studied by determining the point of zero charge (PZC) value of chitosan coated perlite beads using standard potentiometric method. The PZC for beads was found to be 8.5 [40]. The surface charge was almost zero in the pH range of 6–8.5. It increased slowly in the pH range of 3–4.5 due to the protonation of the amine groups suggesting that perlite might have slowed it down. At pH between 4.5 and 8.5, the surface charge of the bead slowly decreased indicating slow protonation of chitosan. Therefore, more NH_2 groups were available to bond with Cu^{2+} ions. Jha et al. [41] also reported a PZC value of 8.5 for chitosan flake. However, Udaybhaskar et al. [42] reported a PZC value in the range of 6.2–6.8 for pure chitosan. The PZC value of 8.5 and the behavior of surface charge of the bead could have been due to the modification of chitosan when coated on perlite, which makes it amphoteric in nature.

The species formed by hydrolysis of copper salt are discussed by Chu and Hashim [43] and Baes and Mesmer [44]. The main hydrolyzed copper species in the pH range of 3–6 appear to be Cu(II) (unhydrolyzed species), $\text{Cu}(\text{OH})^+$, and $\text{Cu}(\text{OH})_2^{0-}$. Among them Cu(II) is the predominant species in the solution within this pH range. Amine groups in chitosan are generally considered as the main active sites for adsorption of metal ions. In the pH range of 2–4.5, both Cu(II) and H^+ ions were present. However, Cu(II) was able to compete better for the active sites. Possible bonding mechanism of bead with copper is given in Fig. 6(d–f). The theoretical amount of $-\text{NH}_2$ for metal binding sites on chitosan is estimated to be about 6.9 mmol/g based on the molecular weight. However, the amount of Cu(II) adsorbed on chitosan is about 5.12 mmol/g of chitosan. Therefore, it is unlikely that two chitosan molecules were involved in chelating or binding with Cu(II). As noted by Monteiro and Airoidi [45], monomer of chitosan can participate in copper adsorption as shown in Fig. 6(e). Also, it appears that some copper may have been adsorbed as $\text{Cu}(\text{OH})^+$. Fig. 6 shows all these mechanisms for copper adsorption by chitosan.

3.4. XPS analysis of beads

Although an experiment was continued for more than 10 h, for XPS study, beads were removed from the solution after

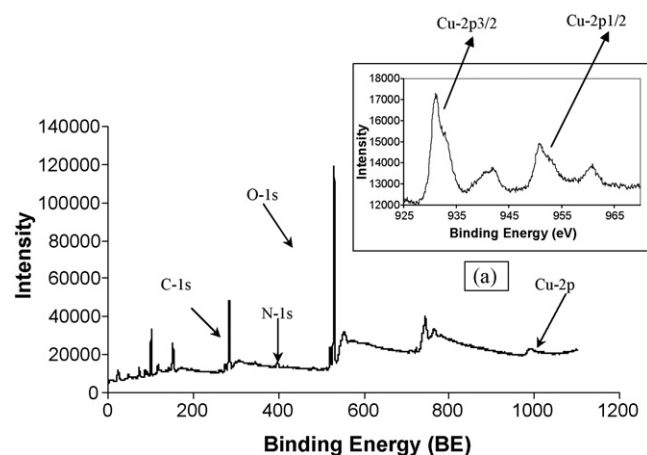


Fig. 7. Survey scan of chitosan coated perlite beads exposed to CuSO_4 .

1 h of exposure, dried at room temperature and kept in desiccators before further analysis. The XPS data were obtained using a KRATOS model AXIS 165XPS spectrometer with a non-monochromatic magnesium X-rays ($h\nu = 1253.6$ eV) used as the excitation source at a power of 240 W. The spectrometer is equipped with an 8-channel hemispherical detector, and the pass energy of 5–160 eV was used during the analysis of samples. Each sample was exposed to X-rays for the same period of time and intensity. The XPS system was calibrated using peaks of UO_2 ($4f_{7/2}$), whose binding energy is 379.2 eV. A zero degree probe angle was used for the analysis of samples.

Fig. 7 shows the peak positions of carbon, oxygen, and nitrogen present in chitosan. These peaks were observed in the same position for flakes, pure chitosan beads, and chitosan coated perlite beads. The C-1s peak observed at 284.3 eV with full width at maximum height (FWHM) of 3.27 showed two peaks on deconvolution, one for C–N at 284.3 eV and the other one for C–C at 283 eV. In chitosan coated perlite beads, the C-1s peak was observed at 283.0 eV compared to 284.3 eV for chitosan flakes (see Table 3). Chemical shifts are considered significant when they exceeded 0.5 eV [40]. However, the shift of 1.3 eV may be due to interaction of C in chitosan with Si and Al in the perlite. The FWHM for all peaks from chitosan coated perlite beads was found to be wider than chitosan flake. This indicates that functional groups of chitosan (amino and hydroxyl) may have formed a complex through cross-linking with constituent of perlite, as shown in Fig. 6(b and c), during the coating process as suggested by Boddu et al. [20].

The XPS analysis of chitosan coated perlite beads that were exposed to copper solution showed peaks at 932 eV that corresponded to Cu (see Fig. 7(a)). Although the kinetic energy of Cu-2p core-level is comparatively small (KE: 320 eV), it is frequently studied because of its great sensitivity compared to other core-level electrons [46]. The Cu-2p spectrum of the sample showed two main peaks; one around 932 eV for Cu-2p_{3/2} and another one at 952 eV for Cu-2p_{1/2}. These two peaks are fingerprints of two valences. The presence of two additional satellite bands in the region of 941–946 and 961–965 eV occurs when the electronic configuration is unsaturated [47]. Cu-2p core-level

Table 3
Absolute binding energy of various elements and copper to chitosan coated perlite bead

Sample	C		N		O	
	BE	Atomic concentration (%)	BE	Atomic concentration (%)	BE	Atomic concentration (%)
Chitosan flake	284.3	67.28	397.5	5.1	530.5	27.06
CP bead	283	57.61	397	3.91	530.5	28.11
Exposed CP bead	283	55.36	398	3.45	530.5	35.6

BE: Binding energy, CP: chitosan coated perlite.

spectrum is generally characterized by the presence of a strong satellite peak. However, the occurrence of two weak satellite peaks was noted, indicating the presence of Cu(II) in the layers close to the surface. Cu-2p_{3/2} lines calibrated with standard samples were found at binding energies of 932.4, 933.4, and 934.8 eV for oxidation states of 0, +1, and +2, respectively [48]. The Cu-2p_{3/2} peaks obtained from this study composed of peaks around 932, 933, and 934 eV. As mentioned earlier, a number of copper hydrolyzed products could be present in the solution. Since chitosan has the capability to adsorb both cationic and anionic species, it is not surprising to observe the presence of all three valence states in the beads. Sorption mechanisms reported by different studies showed that amino groups are main metal binding sites. Both amine and hydroxyl groups presence in the chitosan structure may also form coordination bond with transitional metal ions, which vary with pH of the solution, metal concentration, molecular weight and degree of acetylation of chitosan [29,48,49]. From the C-1s, O-1s, and N-1s core-level

spectra of chitosan flake, chitosan perlite beads, and the beads exposed to copper shown in Fig. 8, it may be noted that N-1s spectrum has significant shift in binding energy compared to C-1s and O-1s spectra. The spectra of C-1s and O-1s of chitosan flake are similar to the spectra of the beads exposed to copper ion as they did not show any noticeable change in the position of binding energy. This data indicates that carbon and oxygen containing functional group had limited participation in metal binding reaction. It is assumed that copper ion entered into the porous matrix of the bead and formed coordination complexes with functional (–NH₂) groups in chitosan by donating electrons to the copper center. Li and Bai [29] also observed same uptake mechanism for copper with cross-linked chitosan bead. It is observed from Table 3 that atomic concentration of oxygen is higher in the beads exposed to copper solution compare to the unexposed beads. As shown in Fig. 6(e), copper might have attached to H₂O during binding, which may have increased the oxygen content in the bead.

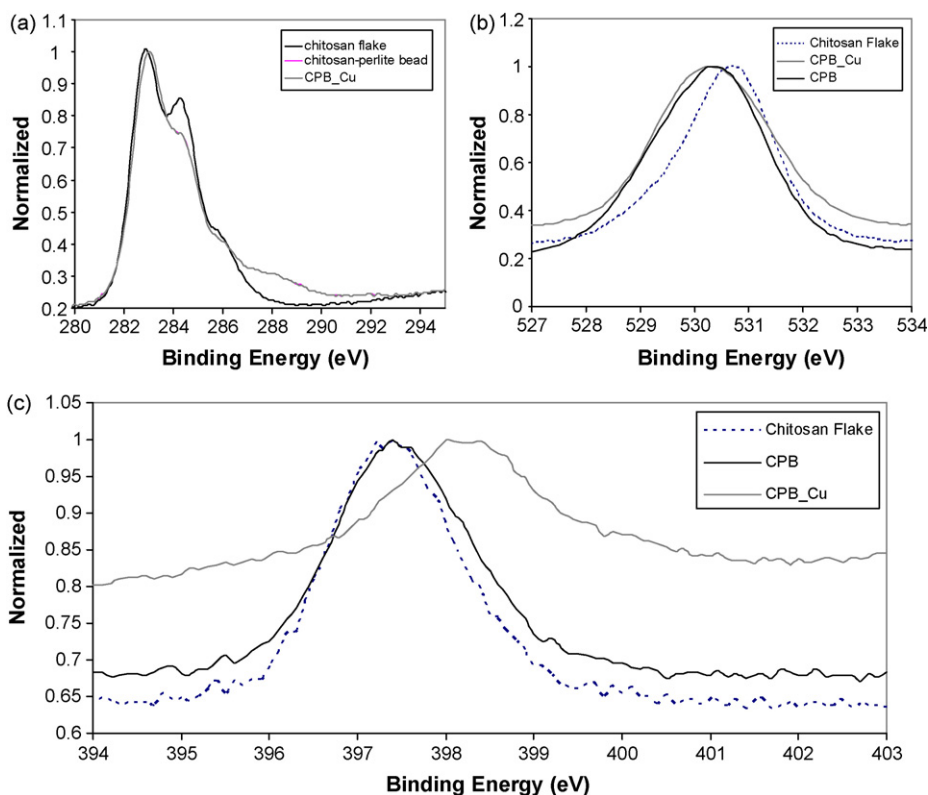


Fig. 8. XPS spectra of (a) C-1s, (b) O-1s, and (c) N-1s for chitosan flake, chitosan perlite beads (CPB) and the beads following exposure to copper sulfate solution.

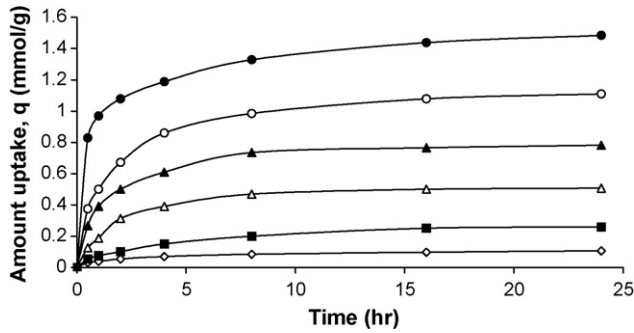
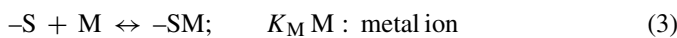
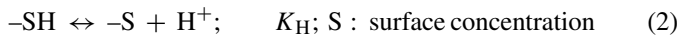


Fig. 9. Effect of time and concentrations on copper(II) uptake by chitosan coated perlite beads. The initial solution concentrations were (●) 64.1, (○) 37.5, (▲) 12.5, (△) 7.81, (■) 3.91, (◇) 1.56 mmol/L.

3.5. Equilibrium adsorption studies

As mentioned in the previous section, chitosan coated beads provided best capacity for Cu(II) ions at a pH 4.5 without any precipitation of Cu(II) from the solution. Therefore, the adsorption isotherm of copper was obtained at pH 4.5 by varying the initial concentration of Cu(II) in the solution in the range of 50–4100 mg/L (0.78–64.1 mmol/L) at 298 K. It was also observed that almost 60% of copper was adsorbed during the first 1 h of a run and the equilibrium was reached around 10 h in most of the runs. An exposure time of 24 h was used during batch studies to ensure that the equilibrium was attained (see Fig. 9).

The adsorption isotherm data obtained at 298 K and pH 4.5 exhibited typical Type I shape indicating monolayer coverage. The uptake of Cu(II) increased monotonically as its concentration in the solution increased, and finally reached its saturation capacity at a higher concentration. Chitosan contains amino and hydroxyl groups that are available for characteristic coordination bonding with metal ions. Adsorption of metal and H^+ ions on chitosan may be described by the one-site Langmuir equation. The effect of pH was incorporated by introducing a parameter “ α ” that is dependent on pH of the solution. The expression is given below [40]:



$$q = \frac{q_m \alpha K_M [M]}{1 + \alpha K_M [M]}; \quad (4)$$

Table 4
Constants of the langmuir equation for copper adsorption on chitosan coated perlite beads at different temperatures

Temperature (K)	Initial solution concentration (mmol/L)	Maximum uptake (mmol/g)		K_m	α	Absolute error (%)	Maximum positive error (%)	Maximum negative error (%)
		q_m	q'_m					
293	0.78–15.6	1.63	1.626	1.2504	0.15	3.324	0.08	10.3
298		1.59	1.593	1.0954		2.86	5.31	4.1
303		1.56	1.567	0.8571		1.55	3.51	1.44
313		1.45	1.44	0.5772		6.29	8	7.95

$$\text{Error} = \left(\frac{\text{experimental} - \text{calculated}}{\text{experimental}} \right) \times 100.$$

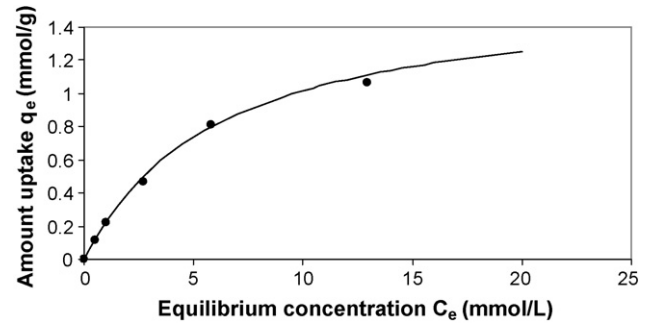


Fig. 10. A comparison of the experimental data with the predicted values from the Langmuir equation for copper(II) uptake on chitosan coated perlite beads at 298 K (solid line is theoretical data and ● experimental data).

$$\alpha = \frac{K_H}{K_H + [H^+]} \quad (5)$$

where q is the adsorption capacity corresponding to metal ion concentration $[M]$, q_m the maximum adsorption amount of metal ions (mmol/g), $[H^+]$ the hydrogen ion concentration, K_H and K_M are equilibrium concentration.

The equilibrium data were correlated with the Langmuir equation (Eq. (4)) within $\pm 5\%$ of experimental value and are shown in Fig. 10. A non-linear regression method was used to obtain the constants and is presented in Table 4.

3.6. Effects of anions on the uptake of copper by beads

The effect of sulfate, chloride, and nitrate anions on copper adsorption was studied at pH of 4.5. These anions are usually present in industrial wastewater and can interfere with the removal of copper. Experiments were carried out in the concentration range of 0–0.1 M of these anions, and the results are shown in Fig. 11. Chloride and nitrate anions did not suppress copper uptake by chitosan coated perlite beads significantly. The adsorption capacity for copper decreased only by 5% in the presence of chloride, and 3% in the presence of nitrate when anion concentration was 0.1 M, and the initial concentration of copper was 100 mg/L (1.56 mmol/L). In these experiments copper sulfate was used for copper ion source. When sodium sulfate was used, as a source of sulfate ions, the uptake of copper was found to reduce by 5%. As noted by Navarro et al. [49], at pH 4.5 more than 99% amine group can undergo protonation. Therefore, it is expected that some anions would bind with amine groups. However, as noted earlier, Cu^{2+} effectively competes with H^+ and occupied amine groups.

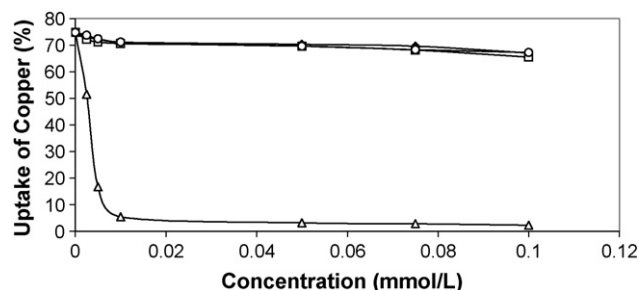


Fig. 11. Effect of various anions on copper(II) uptake by chitosan coated perlite beads. The sodium salt of (◆) Cl, (□) SO₄, (△) EDTA, and (○) NO₃ were used in presence of 1.56 mmol/L (100 mg/L) of CuSO₄ solution.

Fig. 12 shows copper ion distribution in the solution in the presence of EDTA as calculated from MINEQL software. It was noted that the concentration of hydrolyzed species of copper, particularly that of free copper ions decreased significantly in the presence of EDTA. EDTA and copper ions can form complexes rather rapidly, even in a simple 1:1 stoichiometry, and this complex is generally stable. As a consequence, a rapid reduction in copper uptake was also noted when the concentration of EDTA was increased from 0.01 to 0.1 mol/L. This phenomenon, reduction of adsorption capacity of copper, was exploited for regeneration of chitosan coated beads during dynamic studies.

3.7. Dynamic studies

An all-glass column, 2.54 cm in diameter, was used for studying adsorption of Cu(II) under dynamic conditions. The effect of both flow rate and bed height was studied. About 35 g beads were required to make a bed height of 25.4 cm (10 in.). In all the experiments, concentration of Cu(II) was 64.1 mmol/L (4100 mg/L). Increased concentration of Cu(II) was used to expedite the breakthrough time so that a number of cycles can be repeated. Each run was continued for about 180 min and samples at the bed outlet were collected at a 15-min time interval. The bed became saturated during this time period as indicated by the outlet Cu(II) concentration. As can be seen from Fig. 13, at a higher flow rate as the residence time in the column decreased, a faster breakthrough of copper from the column was observed. Although copper broke through the column rather quickly when the inlet concentration was about 64.1 mmol/L (4100 mg/L), it took about

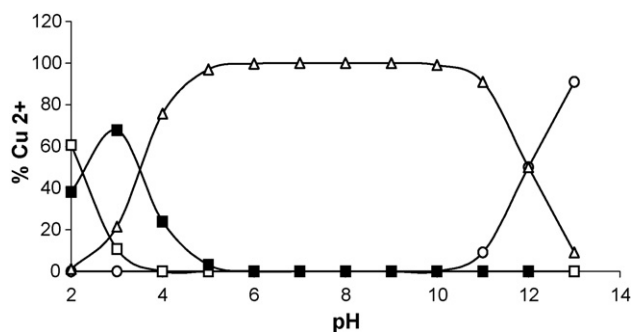


Fig. 12. Distribution of Cu–EDTA species in aqueous solution at different pH. The plot shows the presence of various copper–EDTA complexes in the solution: (○) CuOH–EDTA, (△) Cu–EDTA, (□) CuH₂–EDTA, and (■) CuH–EDTA.

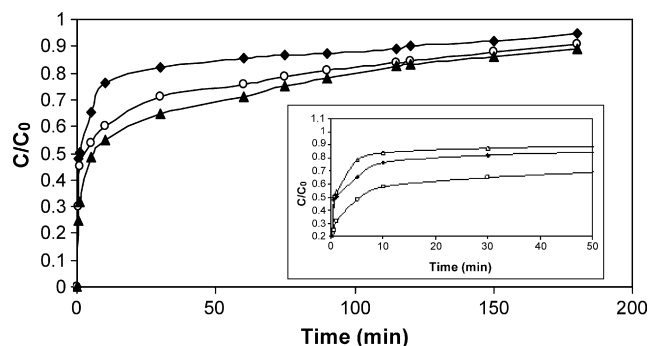


Fig. 13. Effect of flow rate on the breakthrough curve for copper from a column packed with chitosan coated perlite beads. The bed height of the column was 25.4 cm. The inlet influent flow rate was (◆) 10 mL/min, (○) 7 mL/min and (△) 5 mL/min. The inlet influent concentration was 64.1 mmol/L (4100 mg/L).

180 min to saturate the bed at which point the outlet concentration became same as the inlet concentration.

Breakthrough curves were also obtained at two different bed depths, 17.78 and 25.4 cm. Copper concentration in the inlet stream was maintained at 4100 mg/L, and the flow rate through the column was 10 mL/min. The breakthrough curves obtained using two different bed depths are shown in Fig. 14. As can be seen from the figure, a sharp breakthrough curve was not obtained. This suggests that pore diffusion was rate controlling.

3.8. Regeneration using EDTA solution

Although chitosan exhibited excellent adsorption capacity for Cu(II), its removal from the bed was challenging. A stronger concentration of HCl (1N) could not be used due to the disintegration of beads.

Three adsorption–desorption cycles were conducted in which sodium salt of EDTA with different concentrations was used for desorbing copper from the bed (see Fig. 15). The concentrations of EDTA in water were 0.01 and 0.05 mol/L. Almost 96% of the adsorbed copper ions were recovered after first cycle. Approximately 200 mL of EDTA solution was required to regenerate the bed when its concentration was 0.01 mol/L. It took about 1 h to regenerate the column. In the third cycle

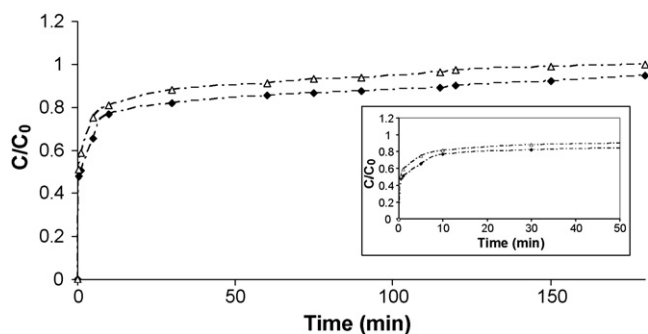


Fig. 14. Effect of bed height on breakthrough curves for copper from a column packed with chitosan coated perlite beads. The inlet influent flow rate was 10 mL/min and the bed heights were (△) 17.78 cm (7 in.) and (◆) 25.4 cm (10 in.). The concentration of copper in the solution was 64.1 mmol/L (4100 mg/L).

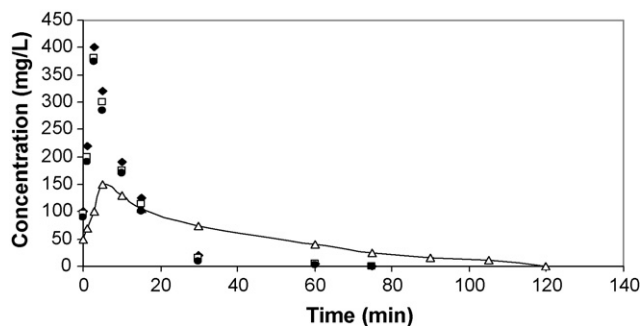


Fig. 15. Regeneration of the bed using 0.05 M (data from three cycles: ◆, □, ●) and (△) 0.01 M EDTA solution.

about 60 mL of 0.05 mol/L EDTA solution was used to regenerate the same column. However, the adsorption efficiency of the bed decreased following regeneration with 0.05 mol/L EDTA compared to regeneration with 0.01 mol/L solution. This was due to the failure to wash the bed completely by water following regeneration with EDTA. As noted earlier, a small amount of EDTA in the solution can reduce the adsorption capacity significantly.

3.9. Calculation of diffusion coefficient from breakthrough curves

Chitosan coated perlite particles were rather non-homogeneous. Chitosan which provides the active sites for adsorption was non-uniformly distributed on perlite. A direct approach, such as the use of Fick's equation could not be used for calculating diffusion coefficient using the batch adsorption data. Therefore, the data from breakthrough curves were used for calculation of diffusion coefficient. The XPS data and the shape of the breakthrough curves suggested that the pore diffusion was the controlling mechanism. Hall et al. [50] developed a model for adsorption of gas or vapor on solid adsorbent assuming pore diffusion and provided a solution both in tabular and graphical forms. They used the Langmuir isotherm equation to describe the equilibrium distribution between the gaseous and solid phases. The one-site Langmuir model (Eq. (4)) provided a good correlation of the batch adsorption data for the entire range of concentration. However, it was noted that the classical Langmuir equation fitted the data equally well for the concentration range used in the dynamic study. Therefore, the model proposed by Hall et al. that used classical Langmuir equation was employed to calculate diffusion coefficient. The solution is given by Eq. (6). Although in the present study the adsorption was from the liquid phase, based on the batch adsorption and dynamic breakthrough data it is concluded that adsorption was physico-chemical in nature and the model of Hall et al. [50] is also applicable here.

$$\frac{15R}{[R + (1 - R)X]^2} \frac{\partial X}{\partial NT} = \frac{\partial^2 X}{\partial R^2} + \frac{2}{R} \frac{\partial X}{\partial R} \quad (6)$$

$$\frac{\partial X}{\partial R} = 0 \quad \text{at } R = 0 \text{ and } X(R, t = 0) = 0$$

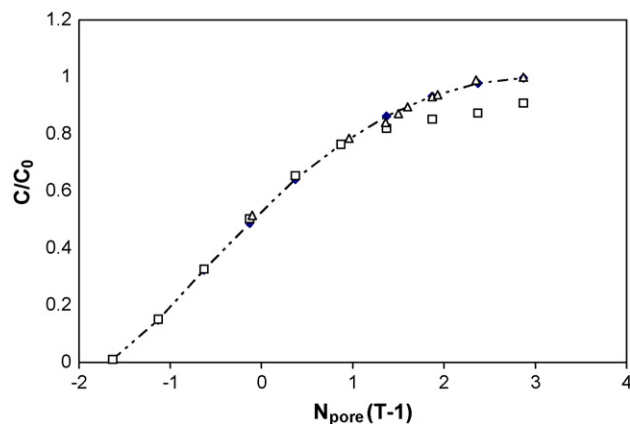


Fig. 16. A comparison between the predicted values obtained using Eq. (5) and the experimental data for copper adsorption in a column packed with chitosan coated perlite beads. The bed height of the column was (□) 25.4 cm and (△) 17.8 cm. The dashed line represents the calculated breakthrough curve from Eq. (5).

Table 5

Diffusion coefficient for adsorption of copper on chitosan coated perlite beads when inlet concentration of copper was 64 mmol/L or 4100 mg/L

Bed height (cm)	Flow rate (mL/min)	N_{pore}	Diffusivity (cm^2/s)
25.4	10	0.0034	2.07×10^{-8}
25.4	7	0.0048	2.04×10^{-8}
25.4	5	0.0066	2.01×10^{-8}
17.8	10	0.0043	1.99×10^{-8}

A solution of Eq. (6) is provided both in graphical form, X vs. $[N_{\text{pore}}(T - 1)]$ and tabular form by Hall et al. [50]. A trial and error method was used for calculation of the diffusion coefficient from the experimental breakthrough curves using Eq. (6). A value of the diffusion coefficient, D_{pore} , was assumed and Eq. (6) was solved using the graphical form given by Hall et al. [50]. The entire breakthrough curve was calculated. A comparison between the predicted values from Eq. (6) and the experimental data is shown in Fig. 16. The values of the diffusion coefficient calculated from four experimental runs are given in Table 5. As can be seen from the table, the values were fairly constant and the average value of the diffusion coefficient was $2.02 \times 10^{-8} \text{ cm}^2/\text{s}$.

4. Conclusion

Chitosan was coated successfully on an inert substrate perlite and was prepared as spherical beads of diameter 2 mm. Scanning electron micrographs showed the beads to be porous in nature. The TEM and XPS analysis indicated that amine groups were the main adsorption sites for copper adsorption as ionic copper. Adsorption capacity for Cu(II) was pH dependent and a maximum uptake of 104 mg/g of beads (or 325 mg/g of chitosan; perlite free basis) was obtained at pH 4.5 when equilibrium concentration in the solution was 812.5 mg/L. Anions in the solution had minimal effect on Cu(II) adsorption

by chitosan. EDTA can be used effectively for the regeneration of the bed. Breakthrough data from the column was used to calculate the diffusion coefficients for Cu(II) into the chitosan coated perlite beads and was about $2.02 \times 10^{-8} \text{ cm}^2/\text{s}$.

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