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Removal of Cu(II) from aqueous solutions using chemically modified chitosan

B. Kannamba, K. Laxma Reddy, B.V. AppaRao*

Department of Chemistry, National Institute of Technology Warangal, Warangal 506004, Andhra Pradesh, India

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ABSTRACT

Chemically modified chitosan namely epichlorohydrin cross-linked xanthate chitosan (ECXCs) has been used for the removal of Cu(II) ions from aqueous medium. The influence of various operating parameters such as pH, temperature, sorbent dosage, initial concentration of Cu(II) ions and contact time on the adsorption capacity of ECXCs has been investigated. Thermodynamic parameters namely ΔG°, ΔH° and ΔS° of the Cu(II) adsorption process have been calculated. Differential anodic stripping voltammetric technique was used to determine the concentration of Cu(II) in the test solution before and after adsorption. The nature of the possible adsorbent–metal ion interactions was studied by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The studies showed that the adsorption of Cu(II) on ECXCs strongly depends on pH and temperature. The maximum adsorption capacity was observed at pH 5.0 and the adsorption capacity of ECXCs increased with increasing temperature indicating the endothermic nature of adsorption process. Langmuir and Freundlich adsorption equations were used to fit the experimental data. The adsorption process is found to follow the pseudo-second-order kinetic model. The maximum adsorption capacity was found to be 43.47 mg g^{-1} from the Langmuir isotherm model at 50 °C. During desorption studies 97–100% of adsorbed copper ion is released into solution in presence of 1N EDTA, HCl and H_2SO_4.

1. Introduction

Removal of heavy metals from industrial effluents assumed great significance due to strict environmental regulations. Copper is one of the most widely used metals and Cu(II) ions are reported to be present in metal-bearing industrial effluents. The maximum contaminant level goal for Cu(II) ion in industrial effluents, as suggested by the US EPA is 1.3 mg L^{-1} [1]. To attain this value different remediation techniques have been applied to remove Cu(II) from industrial effluents. Of these, adsorption technique is considered an effective and extensively used one. Several adsorbents of different origin have been used for the removal of Cu(II) from industrial effluents. In recent years many materials of biological origin such as chitosan and modified chitosan have been used as adsorbents to remove heavy metal ions from ground water and industrial effluents [2–4]. Chitosan is a natural biopolymer, obtained by the partial deacetylation of chitin and has the ability to form complexes with heavy metals. The metal binding capacity of chitosan is mainly due to the presence of amine and hydroxyl groups on chitosan chain. However, chitosan is soluble in dilute mineral and organic acids. Therefore, various physical and chemical modifications have been developed to improve the chemical stability of chitosan in acid media and its resistance to biochemical and microbiological degradation [5]. Reagents like 1,1,3,3-tetramethoxypropane, glycerolpolyglycidylether, chloromethyloxirane, glutaraldehyde, ethyleneglycoldiglycidylether, epichlorohydrin, and tri-polyphosphate have been selected as possible cross-linking agents. In order to improve the sorption selectivity and adsorption ability of chitosan for metal ions, a great number of chitosan derivatives have been prepared by grafting new functional groups such as histidine [6], heparin [7], succinic anhydride [8], N,O carboxymethyl [9] through a cross-linked chitosan back bone.

However, the adsorption ability of epichlorohydrin cross-linked xanthate chitosan (ECXCs) for Cu(II) has not been reported in the literature so far. In the present study, epichlorohydrin cross-linked xanthate chitosan (ECXCs) is used as sorbent for the removal of Cu(II) ions from aqueous medium. The addition of thiol group on epichlorohydrin cross-linked chitosan may enhance the interaction with Cu(II) in solution and an increase in adsorption ability of ECXCs for Cu(II) is expected. The influence of experimental parameters such as pH, temperature, sorbent dosage, contact time and initial concentration of Cu(II) on adsorption capacity of ECXCs was studied. The kinetics of copper uptake by ECXCs was tested with respect to first-order model of Lagergren and pseudo-second-order kinetics. The nature of the possible adsorbent–metal ion interactions was studied by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Various

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* Corresponding author. Tel.: +91 986 6575276; fax: +91 870 2459119.
E-mail address: boyapativapparao@rediffmail.com (B.V. AppaRao).

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thermodynamic parameters, such as ΔG°, ΔH° and ΔS° have been evaluated. Langmuir and Freundlich adsorption equations were used to fit the experimental data. Desorption studies were conducted to evaluate the regeneration and reuse of ECXCs.

2. Materials and methods

2.1. Materials

The chitosan flakes (fluka) with average molecular weight 400 kDa and 74% degree of deacetylation was obtained from fluka. Chitosan flakes were used without further purification. Carbon disulphide, epichlorohydrin (1-chloro-2, 3-epoxipropane) and all other chemicals and reagents used in the present study were of analytical grade. Ultra pure water of 0.05 μs conductivity was used to prepare all the solutions.

2.2. Preparation of epichlorohydrin cross-linked xanthate chitosan (ECXCs)

Chitosan flakes were first cross-linked with epichlorohydrin and then chemically modified as xanthate chitosan [7,10]. Chitosan flakes (0.5 g) were suspended in 100 mL of 5% NaOH solution and 4 mL of 50 mM epichlorohydrin solution was added. After stirring at a temperature of 60 °C for 24 h, the product was filtered and washed several times with ultra pure water and ethanol. Cross-linked chitosan flakes (0.5 g) were treated with 25 mL of 14% NaOH solution and 1 mL of CS_2. The mixture was stirred at room temperature for 24 h. The obtained orange product, epichlorohydrin cross-linked xanthate chitosan (ECXCs) in the form of flakes was washed thoroughly with ultra pure water, air-dried and used in all the experiments.

2.3. Characterization of ECXCs

The solid state ^{13}C NMR Spectrum of ECXCs was recorded using a BRUKER DSX-300 solid state NMR spectrometer. The FTIR spectra of ECXCs before and after adsorption of Cu(II) were recorded using Shimadzu 8201PC FTIR Spectrometer with a resolution of 4 cm^{-1}. The dried sorbent, ECXCs before and after adsorption of Cu(II) was ground into powder. For each type of the powder, 1 mg of the powder was blended with 100 mg of IR-grade KBr in an agate mortar and pressed into a tablet. The spectra of the tablets were scanned within the spectral range of 400–4000 cm^{-1}.

X-ray photoelectron spectra of ECXCs before and after adsorption of Cu(II) were obtained by using kratos model AXIS-165 X-ray photoelectron spectrophotometer with Mg K_∞ (1253.6 eV) radiation and sensitivity of 0.1 eV. The X-ray gun was operated at 15 kV and 20 mA. Survey and high-resolution spectra were collected using 40 and 80 eV pass energy, respectively. Computer deconvolution was applied to detect the elemental peaks of copper, oxygen, nitrogen, sulphur and carbon present in the ECXCs.

2.4. Determination of Cu(II) ions

Concentration of Cu(II) ions present in the solution before and after adsorption was determined by using anodic stripping voltammetric technique in the differential-pulse mode (DPASV) at a hanging mercury drop electrode (HMDE) [11–12]. Metrohm model 663VA electrochemical analyser was used for the purpose. Voltammograms of the sample solutions were taken by scanning in the potential range of −0.01 to −0.05 V at a scan rate of 5 mV/s with the deposition potential of −0.24 V and deposition time of 60 s. Acetate buffer of pH 3 and 0.02 M EDTA as supporting electrolyte were used. In order to eliminate the interference due to dissolved oxygen, the sample solutions were purged with nitrogen gas for about 300 s in order to reduce the sample matrix effect the Concentration of Cu(II) ions in the test solution was determined by Standard addition method.

2.5. Adsorption equilibrium experiments

Batch adsorption experiments were conducted using ECXCs as adsorbent in 300 mL reagent bottles containing 100 mL of various concentrations of Cu(II) solution. The bottles were agitated at 100 rpm in a thermostatic shaking incubator to reach the equilibrium. The effect of pH on the adsorption of Cu(II) by ECXCs was studied in the pH range 1.0–5.0 at 30 °C. The solution pH was adjusted to the desired value with dilute HCl or NaOH solution using a pH meter with a resolution of ±0.01 pH. The effect of temperature on adsorption capacity of ECXCs was studied at 20, 30, 40 and 50 °C with the dosage of 0.01 g/100 mL Cu(II) solution at pH 5. The accuracy of the temperature control was ±0.01 °C. The effect of dosage on the adsorption capacity of ECXCs was determined at different dosages in the range 0.05–0.35 g/100 mL of Cu(II) at an initial concentration of 50 mg L^{-1}. The effect of contact time on the adsorption capacity of ECXCs was studied in the range 1–24 h at an initial concentration of 50 mg L^{-1}. Adsorption kinetics was studied using an initial concentration of 100 mg L^{-1} with the sorbent dosage of 0.1 g/100 mL at pH 5. During the kinetics experiment, aliquots of samples were withdrawn at fixed intervals and the concentration of the Cu(II) ions in each of the samples was determined. Adsorption isotherms were studied at various initial concentrations of Cu(II) ion in the range of 10–100 mg L^{-1} and the experiments were conducted at different constant temperatures in the range 20–50 °C. The maximum adsorption capacity was calculated from Langmuir isotherm plot. The amount of Cu(II) adsorbed per unit mass of ECXCs was calculated by using the mass balance equation given in Eq. (1).

$$Q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

where Q_t is the maximum adsorption capacity in mg g^{-1} at time t, C_0 is the initial concentration and C_t is the concentration at equilibrium of Cu(II) solution in mg L^{-1}, V is the volume of the Cu(II) solution in mL and M is the mass of the ECXCs in grams.

3. Results and discussion

3.1. Characterization of ECXCs

Amine and hydroxyl groups of chitosan are the potential functional groups, which complex with toxic metal ions during the adsorption process. In the present study a new thiol group was introduced and cross-linked with epichlorohydrin in order to improve the adsorption capacity and resistance to solubility in acid media. The prepared sorbent, ECXCs was characterized by FTIR, XPS and solid state ^{13}C NMR spectral analysis. Fig. 1 shows the FTIR spectrum of ECXCs. The broad absorption peak around 3443 cm^{-1} is indicative of the existence of —OH and —NH group stretching vibrations. A small shoulder band at 2925 cm^{-1} can be assigned to the asymmetric —CH stretch of methyl group. The appearance of C=O stretch of amide at 1654 cm^{-1} indicates the partial deacetylation of chitosan. A sharp peak at 1072 cm^{-1} is due to C—O stretching of C—O—C bond, which is formed during cross-linking reaction between chitosan and epichlorohydrin. Since —SH stretching frequency band is very weak, the peak corresponding to —SH is not clearly observed in the FTIR spectrum.

The existence of sulphur on ECXCs was confirmed from the XPS spectrum of ECXCs. The XPS spectrum of ECXCs is presented in Fig. 2. It shows the peaks corresponding to carbon, nitrogen, oxygen and sulphur. The 1s electron peaks of nitrogen at 398.62 and 399.72 eV indicate the amine and amide forms of nitrogen,

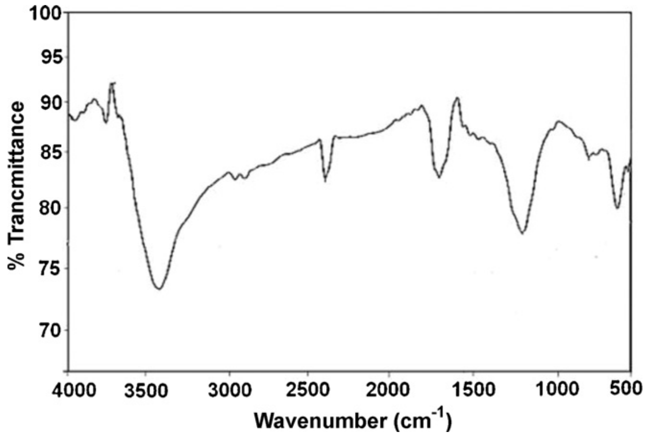

Fig. 1. FTIR spectrum of ECXCs before adsorption of Cu(II).

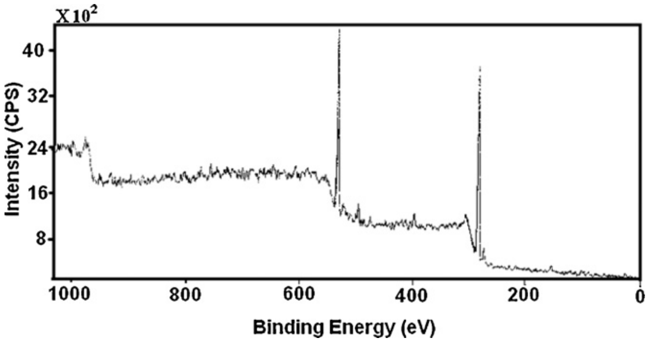

Fig. 2. XPS spectrum of ECXCs before adsorption of Cu(II).

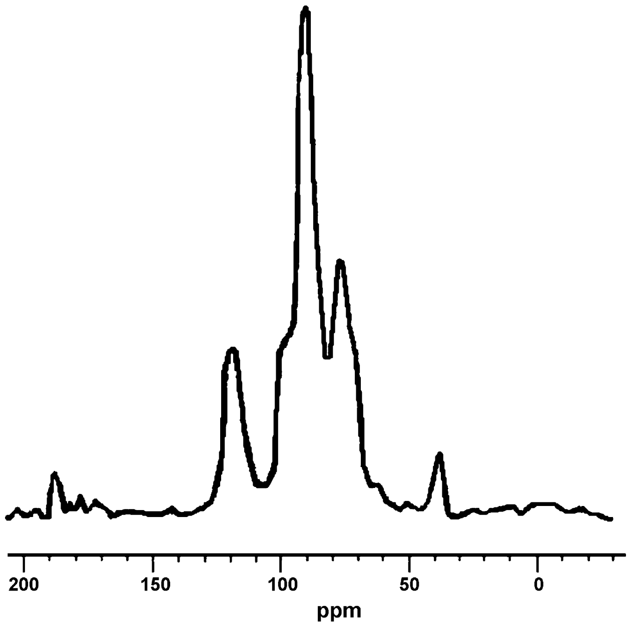

Fig. 3. Solid state ^{13}C NMR spectrum of ECXCs.

respectively. The amide peak of nitrogen appeared due to partial deacetylation of chitosan. The three peaks of carbon 1s at 284.62, 285.87 and 287.36 eV show that carbon binds to three different hetero atoms namely nitrogen, sulphur and oxygen. A peak at 162.94 eV infers the presence of sulphur on the surface of ECXCs. The observed peak at 532.11 eV corresponds to the 1s of oxygen. The solid state ^{13}C NMR spectrum of ECXCs is shown in Fig. 3. The ^{13}C signal at 189.20 EPM corresponds to the carbon atom —C═S functional group of the molecule. This is the most drawn field signal in the spectrum Machiguchi et al. reported the C═S carbon signals at $<\delta = 183$ ppm in ^{13}C NMR spectrum in 2, 4, 6-cycloheptatriene-1-thiones [13]. The most upfield signal at 39.43 ppm is due to carbon atom of the methylene group. The remaining carbon atoms signals of the studied molecule appeared in the usual regions as reported in literature [14]. Thus the molecule is also characterized by the solid state ^{13}C NMR spectrum. Thus, the assigned structure of the prepared sorbent ECXCs is shown in Fig. 4.

3.2. *Effect of initial pH on adsorption capacity of ECXCs*

Effect of initial pH on the adsorption capacity of ECXCs for Cu(II) was studied by varying solution pH from 1 to 5 at the adsorbent dosage of 0.01 g/100 mL using an initial concentration of Cu(II) as 100 mg L^{-1}. The pH range of 1–5 was chosen, as the precipitation of Cu(II) is found to occur at pH ≥6. Variation of adsorption capacity of ECXCs for Cu(II) ions with pH is shown in Fig. 5. It is evident that the adsorption of Cu(II) ions on ECXCs is strongly dependant on the pH of the solution. The adsorption of Cu(II) ions increases steadily with increase in initial pH from 1 to 5 and the maximum adsorption capacity of 13.20 mg g^{-1} is observed at pH 5.0. The functional groups namely —NH$_2$ and —SH of ECXCs are the potential binding sites for chemisorption of Cu(II) ions. The chemisorption of Cu(II) ions and complex formation through —SH group of the adsorbent occur through out the pH range from 1 to 5. However, the amine group is to some extent in the protonated form, NH$_3$$^+$ in the acidic medium. As a result the adsorption capacity of ECXCs for Cu(II) ions is the lowest at pH 1. As the pH of the solution is increased from 1 to 5, the extent of the protonated form of the amino group, i.e., NH$_3$$^+$ decreases and the NH$_2$ form increases [7]. Consequently, the extent of formation of coordination complex between Cu(II) ions and the adsorbent through amino groups increases. As a result, the adsorption capacity increases with increase in pH and reaches a maximum at pH 5. Hence, pH 5.0 is

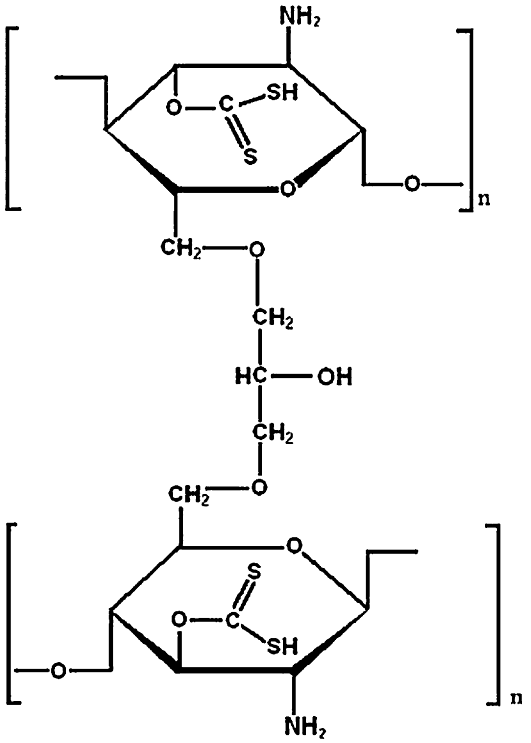

Fig. 4. Structure of epichlorohydrin cross-linked xanthate chitosan.

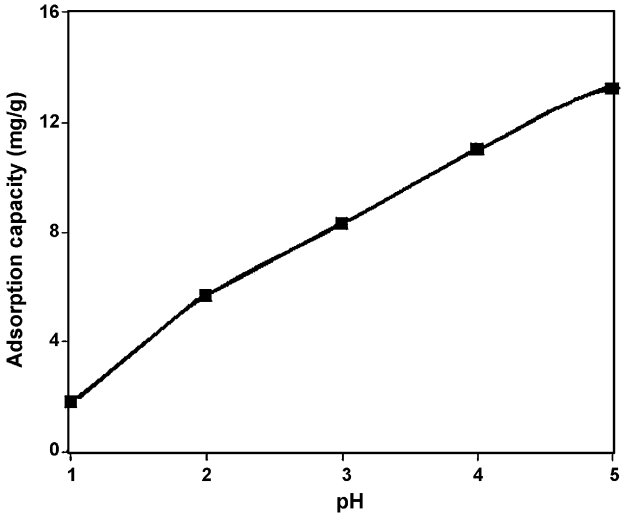

Fig. 5. Effect of pH on adsorption capacity of ECXCs for Cu(II).

fixed as the optimum value for further adsorption studies. In the pH range studied, Cu^{2+} ion is the predominant species of the commonly existing Cu^{2+}, $CuOH^{+}$, $Cu(OH)_2^{0}$,$Cu(OH)_3^{-}$ and $Cu(OH)_4^{2-}$ [5]. It is worth mentioning from the literature reports that the sorbents like heparin treated epichlorohydrin cross-linked chitosan and magnetic Cu(II) ion impregnated composite adsorbent showed the maximum adsorption capacity at pH 5 [7,15].

3.3. Effect of temperature

The effect of temperature on adsorption capacity of ECXCs for Cu(II) ions was studied at pH 5 and the results are shown in Fig. 6. It is observed that the adsorption capacity of ECXCs for Cu(II) ion increases from 12.24 to 14.78 mg g^{-1} with an increase in temperature from 20 to 50 °C. The increase of adsorption capacity of ECXCs for Cu(II) ions with increase in temperature indicates the endothermic nature of the adsorption process. Similar endothermic nature of adsorption was observed by using magnetic Cu(II) ion impregnated composite adsorbent [15]. In general the adsorption process takes place by two consequent processes namely fast diffusion and slow complexation. The increase in temperature not only increases the rate of diffusion of the Cu(II) ions present in the bulk solution to the adsorbent surface but also increases the rate of complexation with the functional groups present in the adsorbent. Further adsorption studies were conducted at the temperature of 50 °C, where the adsorption capacity is found to be the highest.

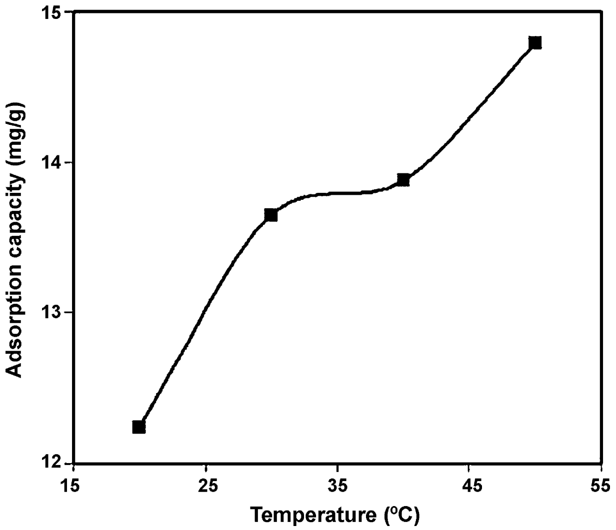

Fig. 6. Effect of temperature on adsorption capacity of ECXCs for Cu(II).

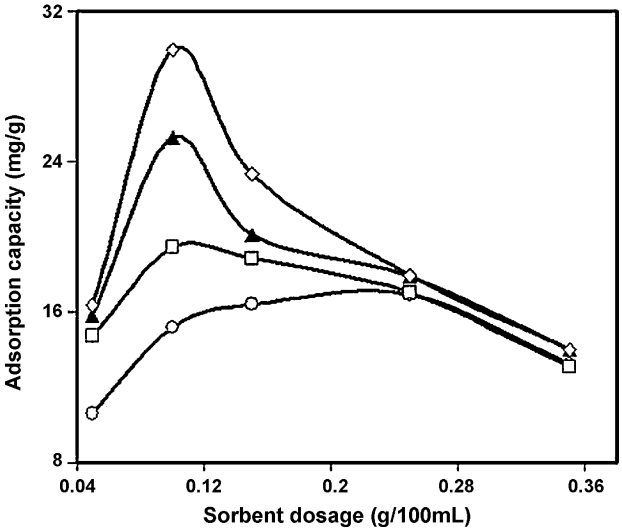

Fig. 7. Adsorption capacity of ECXCs for Cu(II) as a function of adsorbent dosage at different time intervals (○; 6 h), (□; 24 h), (▲; 48 h), (◇; 96 h).

3.4. Effect of adsorbent dosage

The optimum dosage of ECXCs to achieve the highest adsorption capacity was determined at pH 5.0, with the contact time of 24 h and at an initial Cu(II) ion concentration of 50 mg L^{-1}. The amount of ECXCs added to the Cu(II) solutions varied between 0.05 and 0.35 g 100 mL^{-1}. The results of variation of adsorption capacity with the dosage of ECXCs are shown in Fig. 7. Adsorption capacity increases first with an increase in the adsorbent dosage up to 0.1 g and decreases with further increase in the adsorbent dosage. This result infers that 0.1 g of sorbent is sufficient to reach the adsorption equilibrium when the initial concentration of Cu(II) is 50 mg L^{-1}. The decrease in adsorption capacity with increase in the sorbent dosage is mainly because the adsorption equilibrium may not have attained with the sorbent dosage more than 0.1 g and the initial Cu(II) concentration of 50 mg L^{-1}. Further adsorption experiments were conducted with the sorbent dosage of 0.1 g 100 mL^{-1}. Similar results were observed by using saw dust as adsorbent to adsorb Cu(II) ions [16].

3.5. Effect of contact time

After fixing the pH, temperature and sorbent dosage, the effect of contact time on adsorption capacity of ECXCs for Cu(II) ions was investigated at various initial concentrations of Cu(II) ions and the results are presented in Fig. 8. The adsorption capacity increases greatly with the contact time up to 9 h and then onwards increases slightly. The adsorption capacity reaches the equilibrium state with the contact time of 24 h, at all the initial Cu(II) concentrations. However, in the first 6 h, the initial rate of adsorption is greater for higher initial Cu(II) concentration. This is obvious because during initial stage of adsorption a higher concentration gradient is developed, which induces a fast diffusion of Cu(II) from bulk to the adsorbent surface. Similar trend was reported in case of N, O carboxymethyl chitosan, where the equilibration was attained at 22 h of contact time [9].

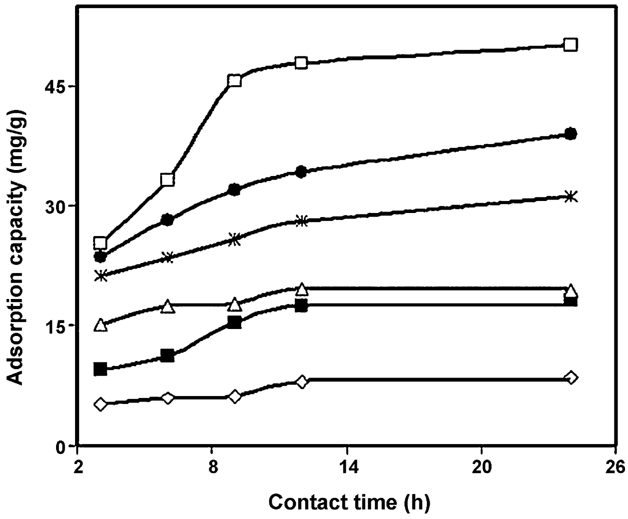

Fig. 8. Effect of contact time on adsorption capacity of ECXCs for Cu(II) at different initial Cu(II) concentrations (◇; 10 ppm), (■; 20 ppm), (△; 40 ppm), (*; 60 ppm), (●; 80 ppm), (□; 100 pm).

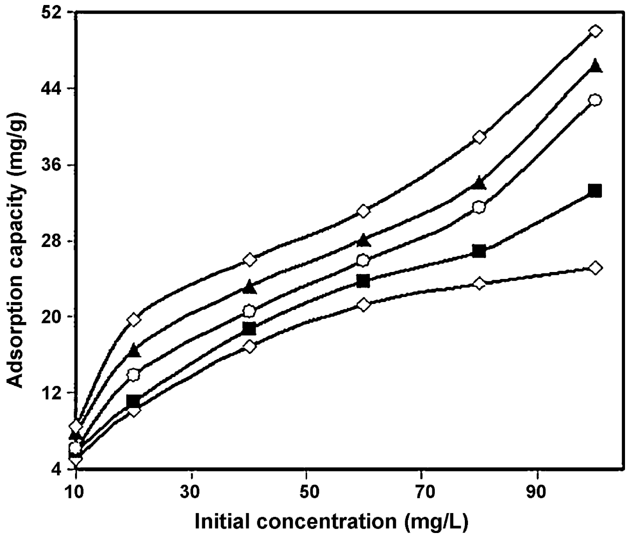

Fig. 9. Effect of initial concentration of Cu(II) on adsorption capacity of ECXCs at different time intervals (◇; 3 h), (■; 6 h), (○; 9 h), (▲; 12 h), (□; 24 h).

3.6. Effect of initial concentration of Cu(II)

Effect of initial concentration of Cu(II) on adsorption capacity of ECXCs was investigated by varying initial concentration of Cu(II) from 10 to 100 mg L^{-1}. For this study, pH, temperature, adsorbent dosage and contact time have been fixed as 5, 50 °C, 0.1 g 100 mL^{-1} and 24 h. The results are presented in Fig. 9. An increase of Cu(II) concentration accelerates the diffusion of Cu(II) ions from solution to the adsorbent surface due to the increase in driving force of concentration gradient. Hence, the amount of adsorbed Cu(II) at equilibrium increased from 7.93 to 47.77 mg g^{-1} as the Cu(II) concentration is increased from 10 to 100 mg L^{-1}.

3.7. Adsorption kinetics

The kinetics of uptake of Cu(II) ions by ECXCs was tested with respect to first-order model of Lagergren and pseudo-second-order kinetic model [17]. First-order model of Lagergren is given in Eq. (2).

$$\log(q_e - q_t) = \log\ q_\mathrm{e} - \frac{k_1 t}{2.303} \tag{2}$$

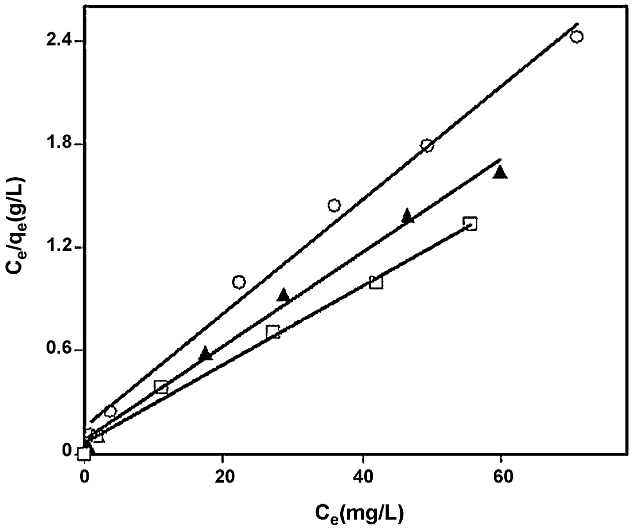

Fig. 10. Langmuir plot for the adsorption of Cu(II) on ECXCs at different temperatures (○; 30 °C), (▲; 40 °C), (□; 50 °C).

In Eq. (2) q_e and q_t are the amounts of Cu(II) ions adsorbed (mg g^{-1}) on the adsorbent at equilibrium and in time t, and k_1 (min^{-1}) is the rate constant. From the slopes of the straight-line plots of log $(q_e - q_t)$ versus t at different temperatures, the values of Lagergren-first-order rate constants k_1 at 30, 40 and 50 °C were calculated.

The pseudo-second-order kinetic equation is expressed in Eq. (3).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

In Eq. (3) q_e^2 is the maximum adsorption capacity (mg g^{-1}) and k_2 (g mg^{-1} min^{-1}) is the adsorption rate constant of pseudo-second-order. Plots of t/q_t against t at different temperatures have been used to obtain the pseudo-second-order rate parameter k_2. The values of k_1 and k_2 at 30, 40 and 50 °C along with the correlation coefficients (R^2) are presented in the Table 1. The correlation coefficients for the pseudo-second-order are higher than those of the Lagergren-first-order. An increase in k_2 with an increase of temperature from 30 to 50 °C is observed. Most of the Cu(II) adsorption studies reported so far were best fitted into the pseudo-second-order model rather than the Lagergren-first-order model [7,15].

3.8. Adsorption isotherms

Langmuir and Freundlich adsorption isotherm models were used to determine the appropriate isotherm for Cu(II) adsorption on ECXCs. The linearized form of Langmuir adsorption isotherm is expressed in Eq. (4).

$$\frac{C_e}{q_e} = \frac{1}{K_\mathrm{L} Q_\mathrm{m}} + \frac{C_e}{Q_\mathrm{m}} \tag{4}$$

In Eq. (4) C_e is the equilibrium concentration of Cu(II) in solution (mg L^{-1}), q_e is the equilibrium concentration of Cu(II) on the adsorbent (mg g^{-1}), Q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir constant and related to the energy of adsorption. The values of Q_m and K_L are determined from the slope and intercept of the plots of C_e/q_e versus C_e at 30, 40 and 50 °C, which are presented in Fig. 10.

The linearized Freundlich isotherm has the general form given in Eq. (5).

$$\log q_e = \log K_\mathrm{F} + \frac{1}{n} \log C_e \tag{5}$$

Table 1

Lagergren-first-order and pseudo-second-order rate parameters for the adsorption of Cu(II) ions on ECXCs at different temperatures.

Temperature (°C)	Lagergren-first-order kinetic model			Pseudo-second-order kinetic model		
	K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
30	2.072×10^{-3}	50.40	0.9896	1.474×10^{-5}	76.92	0.9965
40	2.095×10^{-3}	56.26	0.9905	1.697×10^{-5}	81.30	0.9978
50	2.011×10^{-3}	56.82	0.9919	2.697×10^{-5}	83.33	0.9986

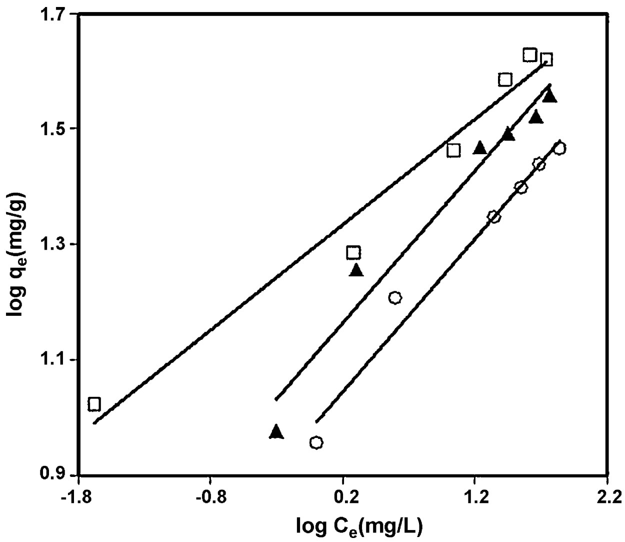

Fig. 11. Freundlich plot for the adsorption of Cu(II) on ECXCs at different temperatures (○; 30 °C), (▲; 40 °C), (□; 50 °C).

In Eq. (5) q_e is the amount of Cu(II) adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of Cu(II) in solution (mg L^{-1}), K_F and n are Freundlich constant and intensity factors, respectively. The values of n and K_F are calculated from slope and intercept of plots of $\log q_e$ versus $\log C_e$ at 30, 40 and 50 °C, which are shown in Fig. 11.

The error analysis of the isotherm constants was done by calculation of Marquardt's Percent Standard Deviation (MPSD). This error function was used previously by a number of researchers in the field [18]. It is similar in some respects to a geometric mean error distribution modified according to the number of degrees of freedom of the system. This error function was calculated by Eq. (6).

$$\mathrm{MPSD} = \sqrt{\frac{1}{n-p}\sum_{i=1}^{p}\left(\frac{q_{e,\mathrm{meas}} - q_{e,\mathrm{calc}}}{q_{e,\mathrm{meas}}}\right)_i^2} \tag{6}$$

where n = the number of data points; p = the number of parameters.

The values of K_L, Q_m, K_F, n and R^2 along with the corresponding values of MPSD are presented in Table 2. The straight line plots of Langmuir and Freundlich adsorption isotherm models indicate that the adsorption of Cu(II) on ECXCs follows both Langmuir and Freundlich isotherms. The higher value of correlation coefficient (R) for Langmuir than for Freundlich isotherm indicates that the experimental adsorption data provided better fit in Langmuir isotherm model. Similar trends have also been observed by Ng et al. [18] for the adsoption of Cu(II) on chitosan, Krishnani et al. for biomatrics of rice husk [19]. As obtained from Langmuir plots, the maximum monolayer adsorption capacity (Q_m) of ECXCs for Cu(II) increases with an increase of temperature and a value of 43.47 mg g^{-1} is obtained at 50 °C. This result is comparable with the adsorption capacity of the other sorbents reported in literature [20,21].

A dimensionless parameter referred to as separation factor/equilibrium parameter (R_L) obtained from Langmuir adsorption isotherm model is used to predict the favourability of adsorption process. R_L is determined by using Eq. (7).

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

In Eq. (7) K_L is the Langmuir constant and C_0 is the initial liquid phase concentration of Cu(II) in equilibrium with the Cu(II) adsorbed on the adsorbent. For a favourable adsorption process the R_L value lies between 0 and 1. The R_L values for adsorption of Cu(II) ions onto ECXCs lie between 0 and 1. Therefore, the adsorption on ECXCs of Cu(II) is said to be favourable process.

3.9. Thermodynamic parameters

In adsorption studies, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. Values of thermodynamic parameters are the actual indicators for practical applicability of a process. The amounts of Cu(II) ions adsorbed at different temperatures 30, 40 and 50 °C, at equilibrium have been used to obtain thermodynamic parameters for the adsorption process. The dependence of Langmuir constant (K_L) with temperature was used to predict the thermodynamic parameters associated with the adsorption process [20]. The standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were

Table 2

Langmuir and Freundlich isotherm constants for the adsorption of Cu(II) ions on ECXCs at different temperatures.

Temperature (°C)	Langmuir isotherm constants			MPSD		
	K_L	Q_m	R^2	K_L	Q_m	R^2
30	0.211	30.21	0.9917	0.402	2.92	0.7125
40	0.342	36.63	0.9939	0.404	3.05	0.7136
50	0.396	43.47	0.9929	0.452	3.36	0.7126
Temperature (°C)	Freundlich isotherm constants			MPSD		
	K_F	n	R^2	K_F	n	R^2
30	9.819	3.779	0.9741	2.42	2.23	0.9520
40	12.92	3.796	0.9629	2.91	2.58	0.9615
50	19.86	5.464	0.9141	3.28	2.81	0.9625

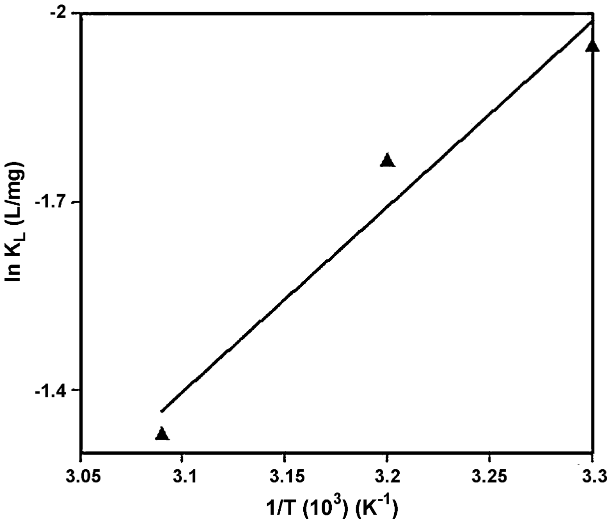

Fig. 12. Plot of $\ln K_L$ against $1/T$ for the adsorption of Cu(II) on ECXCs.

determined by using Eqs. (8) and (9).

$$\Delta G^\circ = -RT \ln K_L \tag{8}$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{9}$$

The plot of $\ln K_L$ as a function of $1/T$ shown in Fig. 12 yields a straight line from which ΔH° and ΔS° are calculated from the slope and intercept, respectively. The values of standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) are presented in Table 3. The overall free energy changes during the adsorption process at 30, 40 and 50 °C are negative, corresponding to a spontaneous and thermodynamically favourable process of adsorption of Cu(II) ions. The positive value of +25.73 kJ mol^{-1} of the enthalpy change indicates that the adsorption is endothermic in nature. Endothermic adsorption of Cu(II) ions on magnetic Cu(II) ion impregnated sorbent has been reported [15]. The entropy change (ΔS°) value of −0.073 J mol^{-1} K^{-1} reflects the affinity of the ECXCs for Cu(II) ions.

3.10. Regeneration of ECXCs

Desortption of Cu(II) from ECXCs was studied by using acids such as H_2SO_4, HCl and a complexing agent EDTA, as regenerants. At a concentration of 0.01 M each of H_2SO_4, HCl and EDTA and with the contact time of 35 min, it is possible to desorb only 69, 64 and 74% respectively of adsorbed Cu(II) ions on ECXCs into the solution. As the concentration of the regenerant is increased to 0.1 M, the desorption of Cu(II) increases to 98, 97 and 91% for H_2SO_4, HCl and EDTA, respectively. When acids are used as regenerants, the amine functional groups on the sorbents are protonated which induce the repulsive force between the adsorbed Cu(II) and NH_3^+ groups and as a result Cu(II) is released into the solution. When the complexing agent, EDTA is used as regenerant, it has strong affinity for the adsorbed Cu(II) and the Cu(II) ions are released into solution in the form of a soluble Cu(II)–EDTA complex.

Table 3
Thermodynamic parameters for the adsorption of Cu(II) ions on ECXCs.

ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (kJ K^{-1} mol^{-1})
30 °C	40 °C	50 °C		
−3.913	−2.787	−2.483	+26.13	−0.07352

3.11. Comparison with the other sorbents

Ng et al. reported the equilibrium studies on chitosan for the removal of Cu(II) ions [18]. Based on fitting the data with Langmuir adsorption isotherm, they found an adsorption capacity of 2.0834 mg of Cu(II)/g of chitosan. They also reported an increase in Cu(II) adsorption capacity with decrease in pH from 4.5 to 3.5. They interpreted it due to ion exchange of the metal ions with hydrogen ions of the protonated amine groups. However, below pH 3.5 the decease in sorption capacity is interpreted in terms of increased probability of H$^+$ ion exchange, competing with the sorbed metal ions. At nearly identical particle size the chemically modified chitosan reported in the present study is found to have high adsorption capacity of 43.47 mg g^{-1} at pH 5 and at a concentration of 100 ppm Cu(II). The present results also showed an increase in adsorption capacity of the adsorbent with an increase in pH from 1 to 5. The mechanism of the adsorption is interpreted in terms of chemisorption of Cu(II) ions on ECXCs and subsequent complex formation with the adsorbent. The present results showed better fit of Langmuir adsorption isotherm in comparison to Freundlich adsorption isotherm. Adsorption of Cu(II) on pure chitosan is also found to obey Langmuir isotherm better than others [18].

Coelho et al. reported the effect of heparin coating on epichlorohydrin cross-linked chitosan microspheres on the adsorption of Cu(II) [7]. These authors prepared microspheres of epichlorohydrin cross-linked chitosan (CS) and chitosan–heparin polyelectrolyte complex microspheres (CHS). Thus the physical state of the adsorbent used by them is totally different from that of the present study, which is in the form of flakes and the surface area or particle size is not comparable. The authors reported maximum adsorption capacity of 39.31 mg g^{-1} for CS and 81.04 mg g^{-1} for CHS. They also reported an increase in adsorption capacity with increase in pH from 3 to 6, which was interpreted due to a decease in amine group protonation with increase in pH. Coelho et al. have not reported the desorption studies of Cu(II) ions from CS or CHS adsorbent.

Zhou et al. studied adsorption of Cu(II) ions by thiourea-modified magnetic chitosan microsheres (TMCS) [22]. In this case also the physical state of the adsorbent is different from the one used in the present study. They reported that Langmuir isotherm correlated better than Freundlich and Temkin isotherms. They calculated the maximum adsorption capacity of 66.7 mg g^{-1} when the Cu(II) ion concentration is in the range of 25–350 mg L^{-1}. They also found an increase in adsorption capacity with increase in pH from 1 to 6. The prepared sorbent was desorbed by using EDTA.

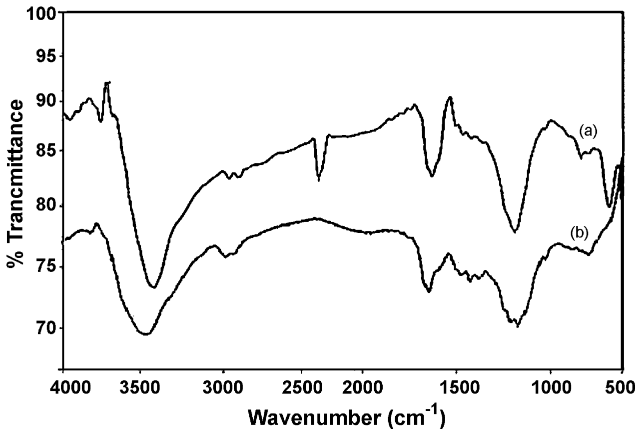

Fig. 13. FTIR spectra of ECXCs (a) before adsorption and (b) after adsorption of Cu(11).

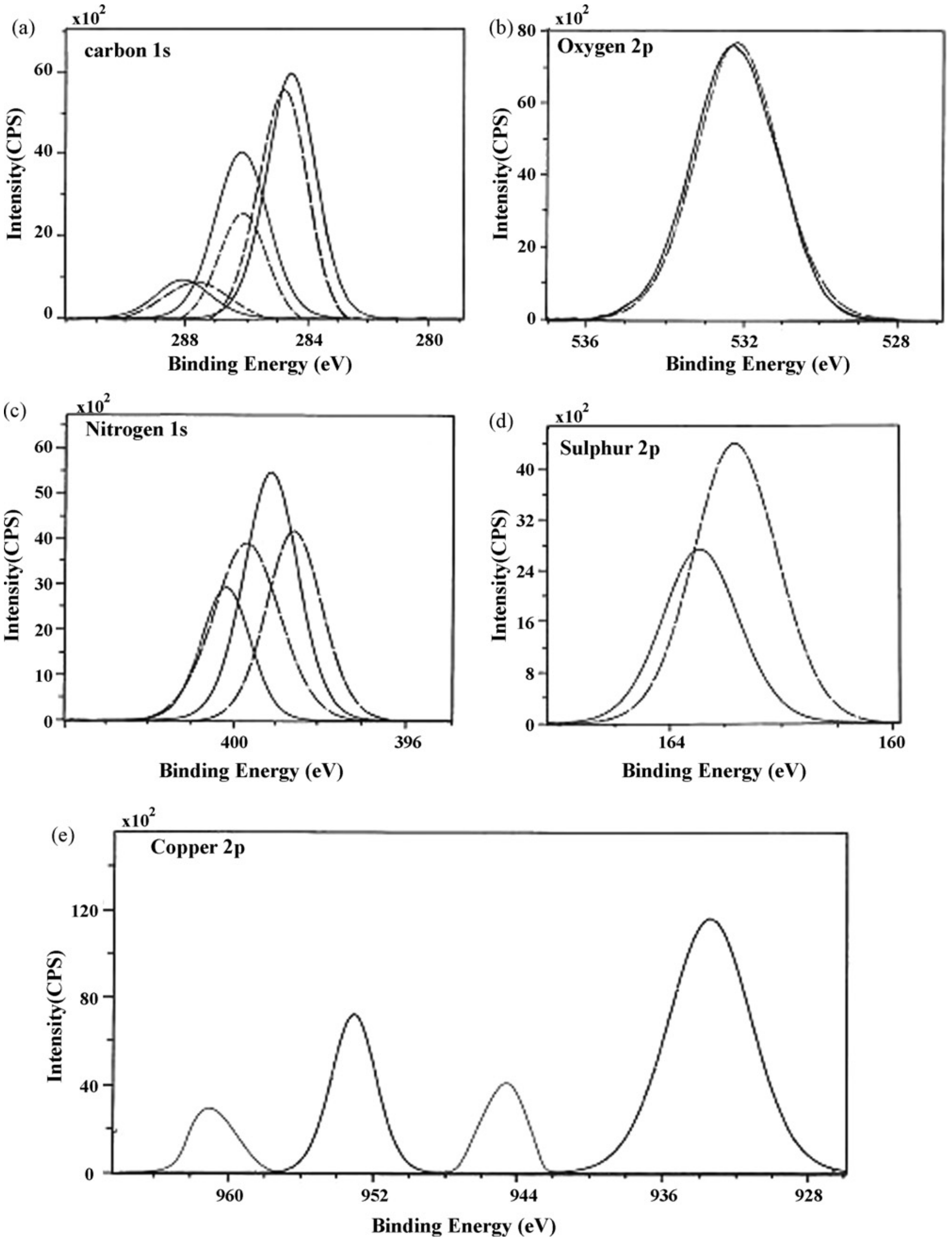

Fig. 14. Computer deconvolution spectra of (a) C 1s, (b) O 2p, (c) N 1s, (d) S 2p and (e) Cu 2p. (– – – before adsorption of Cu(II), ––– after adsorption of Cu(II).

Vasconcelos et al. studied the use of chemically modified chitosan by cross-linking with a complexing agent (N-N-[bis(2-hydroxy-3-formyl-5- methylbenzyl dimethyl)]-ethylene diamine) (H_2 fmbme) for removal of Cu(II) ions [21]. They reported a dramatic increase in Cu(II) adsorption by CHS—H_2 fmbme to an extant of one and half times as the pH is increased from 5 to 6. They interpreted the increase in adsorption capacity due to complexation between Cu(II) and the ligand. However, they have not reported any desorption studies, in the absence of which the adsorbent has limited practical applications.

Beppu et al. reported studies on adsorption of Cu(II) on porous chitosan membranes functionalized with histidine [6]. They prepared highly porous epichlorohydrin cross-linked chitosan membranes on which histidine was immobilized. They showed the maximum adsorption capacity of 2.0–3.0 mmol of Cu(II)/g of chitosan depending upon the porosity of membrane. Nevertheless, they have not reported any desorption studies.

Ngah et al. reported the adsorption capacities of chitosan beads and various chemically cross-linked chitosan beads using the reagents namely ethylene glycol diglycidylether, glutaraldehyde and epichlorhydrin as 80.7, 45.9, 59.7 and 62.5 mg g^{-1} of the adsorbent. They also reported that aqueous EDTA solution was the regenerant [23]. The literature reports also showed an adsorption capacity of 117 mg g^{-1} on the cross-linked N-Succinyl-chitosan [24] and of 136–155 mg g^{-1} on the cross-linked carboxymethyl-chitosan under different conditions [25]. It must be noted here that only under identical conditions such as the physical state of the sorbent, surface area or particle size, concentration of Cu(II) ions, dosage of the sorbent and temperature, the adsorption capacities of different adsorbents must be compared. Moreover, for applications in waste water treatment it is necessary that the adsorbed Cu(II) ions must be desorbed by a suitable desorbent with greater efficiency. Otherwise, the advantage of higher adsorption capacity is offset by the disadvantage of less desorption of the adsorbed Cu(II) ions.

3.12. Mechanism of adsorption of Cu(II)

The FTIR spectra of ECXCs before and after adsorption of Cu(II) ion are shown in Fig. 13. After adsorption of Cu(II) on ECXCs, a shift of adsorption bands at 3443, 1654, 1122 $\mathrm{cm^{-1}}$ corresponds to —NH, —C═O and —C—O— stretching frequencies. Such shifts indicate that the nitrogen of ECXCs is involved in chemisorption of Cu(II) and subsequent complexation process. Appearance of a sharp peak at 601 $\mathrm{cm^{-1}}$ is assigned to the stretching vibration of N—Cu bond formed during complexation process. Fig. 14 shows the computer deconvolution XPS spectra of C 1s, O 1s, N 1s, S 2p and Cu 2p before and after adsorption of Cu(II) ions on ECXCs. The computer deconvolution spectrum of Cu(II) shows two peaks, one peak at 933.60 eV and another at 953.07 eV along with their weak satellite peaks around 944.20 and 960.80 eV respectively. The standard $\mathrm{Cu2p_{3/2}}$ electron binding energies of 932.4, 933.4 and 934.6 eV correspond to the elemental copper, cuprous and cupric forms respectively [26]. More over the weak satellite peaks denote the presence of Cu(II) ions [26]. The observed binding energy peak positions of copper 2p electron along with their weak satellite peaks in the spectrum of the present study provide an evidence for the presence of Cu(II) on ECXCs after adsorption. The XPS spectrum of sorbents such as chitosan coated perlite beads and chitosan-cellulose hydrogel bead after the adsorption of Cu(II) ions also shows the binding energy peak for Cu 2p electron at 933.4 eV [27,28]. The computer deconvolution XPS spectra of C 1s and O 1s of ECXCs before and after adsorption of Cu(II) ions indicated that the binding energy positions of C 1s and O 1s did not show any noticeable change after Cu(II) ion adsorption. But the computer deconvolution XPS spectra of N 1s and S 2p show significant binding energy shits. A significant N 1s binding energy shift from 398.62 to 399.14 eV for amine and a shift from 399.77 to 400.20 eV for amide groups of ECXCs are attributed to the involvement of the lone pair of electrons on nitrogen on ECXCs in bond formation with Cu(II) ion. The studies on adsorption of Cu(II) on chitosan coated perlite beads and chitosan-cellulose hydrogel beads also reported the participation of N of amine in complexation with Cu(II) through XPS spectral analysis. The computer deconvolution XPS spectrum of S 2p shows a binding energy shit from 162.94 eV to 163.44 eV after adsorption of Cu(II), which infers that the sulphur of thiol group on ECXCs is involved in chemisorption of Cu(II) ions. The negative charges of -0.485 and -0.0382 on nitrogen and sulphur of ECXCs respectively obtained using Chem3D Ultra software of version 8.0 indicate that the amine and thiol groups of ECXCs are the potential adsorption sites for Cu(II) ions. The FTIR and XPS spectral analysis of ECXCs before and after adsorption of Cu(II) confirm that both nitrogen and sulphur of ECXCs are actively participated during the adsorption process through complexation with Cu(II) ion.

4. Conclusions

Batch adsorption studies showed that the adsorption capacity of ECXCs for the removal Cu(II) ions is strongly dependent on initial pH and temperature. The maximum adsorption capacity of ECXCs was obtained at pH 5.0 and at 50 °C. The adsorption process obeys both the Langmuir and Freundlich adsorption isotherms for over all concentration range studied. Based on a linearized correlation coefficient the Langmuir isotherm model gives better fit than the Freundlich isotherm model. The maximum adsorption capacity of ECXCs for Cu(II) is 43.47 $\mathrm{mg\,g^{-1}}$, as obtained from the Langmuir isotherm plot. The adsorption of Cu(II) ions on ECXCs follows the pseudo-second-order kinetic model. The thermodynamic parameters obtained from Langmuir constant (K_L) indicate that the adsorption process of Cu(II) on ECXCs is spontaneous and becomes more favourable at higher temperature. FTIR and XPS spectral analysis infer that the nitrogen and sulphur in the form of amine and thiol functional groups on ECXCs are involved in complexation with Cu(II) ions. Regeneration studies suggest that the adsorbent ECXCs can be used effectively for a number of adsorption/desorption cycles.

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References

[1] USEPA, Lead and Copper Monitoring and Reporting Guidance for Public Water Systems, EPA-816-R-02-009, Ground Water and Drinking Water Division, Water Programs, US Environmental Protection Agency, Washington, DC, 2002.

[2] H.K. An, B.Y. Park, D.S. Kim, Crab shell for the removal of heavy metals from aqueous solution, Water Res. 35 (2001) 3551–3556.

[3] S. Verbych, M. Bryk, G. Chornokur, B. Fuhr, Removal of copper(II) from aqueous solutions by chitosan adsorption, Sep. Sci. Technol. 40 (2005) 1749–1759.

[4] F. Zhao, B. Yu, Z. Yue, T. Wang, X. Wen, Z. Liu, C. Zhao, Preparation of porous chitosan gel beads for copper(II) ion adsorption, J. Hazard. Mater. 147 (2007) 67–73.

[5] P.O. Osifo, A. Webster, H. van der Merwe, H.W.J.P. Neomagus, M.A. van der Gun, D.M. Grant, The influence of the degree of cross-linking on the adsorption properties of chitosan beads, Bioresour. Technol. 99 (2008) 7377–7382.

[6] M.M. Beppu, E.J. Arruda, R.S. Vieira, N.N. Santos, Adsorption of Cu(II) on porous chitosan membranes functionalized with histidine, J. Membr. Sci. 240 (2004) 227–235.

[7] T.C. Coelho, R. Laus, A.S. Mangrich, V.T. de Favere, M.C.M. Laranjeira, Effect of heparin coating on epichlorohydrin cross-linked chitosan microspheres on the adsorption of copper (II) ions, React. Funct. Polym. 67 (2007) 468–475.

[8] I.S. Lima, C. Airoldi, Interaction of copper with chitosan and succinic anhydride derivative a factorial design evaluation of the chemisorption process, Colloid Surf. A: Physicochem. Eng. Aspects 229 (2003) 129–136.

[9] S. Sun, A. Wang, Adsorption kinetics of Cu(II) ions using *N*,*O*-carboxymethyl-chitosan, J. Hazard. Mater. B131 (2006) 103–111.

[10] L. Tan, D. Zhu, W. Zhou, W. Mi, L. Ma, W. He, Preferring cellulose of *Eichhornia crassipes* to prepare xanthogenate to other plant materials and its adsorption properties on copper, Bioresour. Technol. 99 (2008) 4460–4466.

[11] D. Sancho, M. Vega, L. Deban, R. Pardo, G. Gonzalez, Determination of copper and arsenic in refined beet sugar by stripping voltammetry without sample pre-treatment, Analyst 123 (1998) 743–747.

[12] G. Ekmekci, G. Somer, O. Sendil, Simultaneous determination of copper, zinc and selenium in chicken liver by diferential pulse polarography, Turk. J. Chem. 27 (2003) 347–355.

[13] T. Machiguchi, T. Hasegawa, Y. Kano, General synthesis, spectroscopic properties and dipole moment of 2-substituted tropothiones, Bull. Chem. Soc. Jpn. 66 (1993) 3699–3706.

[14] H. Saito, I. Ando, A. Naito, Solid State NMR Spectroscopy for Biopolymers: Principles and Applications, Springer, Dordrecht, 2006, p. 301.

[15] Y. Ren, X. Wei, M. Zhang, Adsorption character for removal Cu(II) by magnetic Cu(II) ion impregnated composite adsorbent, J. Hazard. Mater. 158 (2008) 14–22.

[16] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. 95 (2002) 137–152.

[17] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.

[18] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interface Sci. 255 (2002) 64–74.

[19] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Boddukrishnani, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater. 153 (2008) 1222–1234.

[20] O. Gok, A. Ozcan, B. Erdem, A.S. Ozcan, Prediction of the kinetics, equilibrium and thermodynamic parameters of adsorption of copper(II) ions onto 8-hydroxy quinoline immobilized bentonite, Colloids Surf. A: Physicochem. Eng. Aspects 317 (2008) 174–185.

[21] H.L. Vasconcelos, T.P. Camargo, N.S. Goncalves, A. Neves, M.C.M. Laranjeira, V.T. Favere, Chitosan cross-linked with a metal complexing agent: synthesis, characterization and copper(II) ions adsorption, React. Funct. Polym. 68 (2008) 572–579.

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

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

[24] S. Sun, A. Wang, Adsorption properties of *N*-succinyl-chitosan and cross-linked *N*-succinyl-chitosan resin with Pb(II) as template ions, Sep. Purif. Technol. 51 (2006) 409–415.

[25] S. Sun, A. Wang, Adsorption properties of carboxymethyl-chitosan and cross-linked carboxymethyl-chitosan resin with Cu(II) as template, Sep. Purif. Technol. 49 (2006) 197–204.

[26] S. Biniak, M. Pakula, G.S. Szymanski, A. Swiatkowski, Effect of activated carbon surface oxygen and/or nitrogen containing groups on adsorption of copper(II) ions from aqueous solution, Langmuir 15 (1999) 6117–6122.

[27] S. Hasan, T.K. Ghosha, D.S. Viswanath, V.M. Boddub, Dispersion of chitosan on perlite for enhancement of copper(II) adsorption capacity, J. Hazard. Mater. 152 (2008) 826–837.

[28] N. Li, R. Bai, Copper adsorption on chitosan-cellulose hydrogel beads: behaviors and mechanisms, Sep. Purif. Technol. 42 (2005) 237–247.