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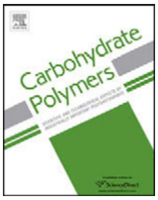

Sorption behaviour of copper on chemically modified chitosan beads from aqueous solution

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ABSTRACT

In order to increase the copper sorption capacity (SC) of raw chitosan beads (CB), they were chemically modified into protonated chitosan beads (PCB), carboxylated chitosan beads (CCB) and grafted chitosan beads (GCB) which showed a significant SC of 52, 86 and 126 mg/g respectively while raw chitosan beads (CB) displayed only 40 mg/g. Among the sorbents studied, GCB experienced a higher SC than CB, PCB and CCB. Sorption experiments were performed by varying contact time, pH, presence of co-anions, different initial copper concentrations and temperature for optimization. The nature and morphology of the sorbents were discussed using FTIR and SEM analysis. The copper uptake onto PCB, CCB and GCB obeys the Freundlich isotherm. Thermodynamic studies revealed that the nature of copper sorption is spontaneous and endothermic.

1. Introduction

Nowadays, biosorption is recognized as an emerging technique for the treatment of waste water containing heavy metals (Wan Ngah, Ghani, & Hoon, 2002). Chitosan, poly (1-4)-2 amino-2-deoxy-β-D-glucan is prepared from chitin by deactylating its acetamido groups with strong alkaline solutions (Jollès & Muzzarelli, 1999). Chitosan appears to be more useful as compared to chitin, since it possesses more number of chelating amino groups and can be chemically modified (Jayakumar, Rajkumar, Freitas, Selvamurugan, et al., 2009; Jayakumar, Rajkumar, Freitas, Sudheesh Kumar, et al., 2009; Rajiv Gandhi, Viswanathan, & Meenakshi, 2010; Wan Ngah, Ghani, et al., 2002).

Chitosan when it is used in powder form, cause pressure drop during filtration. To overcome such technology bottlenecks, it is aimed to prepare chitosan in a usable beads form. Several chemical modifications have been proposed in order to improve pore size, mechanical strength, chemical stability, hydrophilicity and biocompatibility of chitosan beads. Chitosan has been crosslinked to enhance the mechanical strength and chemical resistance. Several cross-linking agents like glutaraldehyde (Wan Ngah, Endud, & Mayanar, 2002; Wan Ngah & Fatinathan, 2008), ethylene glycol diglycidyl ether (Wan Ngah, Endud, et al., 2002), epichlorohydrine (Chen, Liu, Chen, & Chen, 2008; Coelho, Laus, Mangrich, de Favere, & Laranjeira, 2007; Wan Ngah, Endud, et al., 2002) have been reported.

The present investigation aims at the development of modified chitosan beads for copper sorption which is stable and could be regenerated. In order to effectively utilize the amine and hydroxyl groups of chitosan they have been modified into PCB, CCB and GCB so as to enhance the SC. The SC of these modified forms and their comparative studies for Cu(II) have not been reported in the literature.

2. Materials and methods

2.1. Materials

Chitosan with its deacetylation degree of 85% was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). The viscosity of the chitosan solution was determined as 700 (mPa s) by Brookfield Dial Reading Viscometer using electronic drive-RVT model (USA made). The chitosan solution was maintained at a constant viscosity for beads preparation in order to maintain uniform molecular weight. Copper sulphate, NaOH, HCl, glacial acetic acid, glutaraldehyde, ethylenediamine and all other chemicals and reagents were of analytical grade.

2.2. Instrumentation

Copper concentration was measured using the atomic absorption spectrophotometer, Perkin Elmer model AAnalyst 100 at

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wavelength 324.8 nm and slit width as 0.7 (APHA, 2005). Duplicate measurements were made such that the residual concentration values were reproducible within ±2%. The pH measurements were done with an expandable ion analyzer EA 940 with the pH electrode.

FTIR spectra of the sorbents were obtained using JASCO-460 plus model to confirm the presence of functional groups. The surface morphology of the modified chitosan beads before and after copper sorption was studied with scanning electron microscope (SEM) with JOEL JSM 6390 LV model.

2.3. *Preparation of raw and modified chitosan beads*

The raw CB have been prepared and crosslinked as reported in the literature (Jeon & Holl, 2003; Viswanathan, Sairam Sundaram, & Meenakshi, 2009). In order to effectively utilize both –OH and $-NH_2$ groups in chitosan for copper removal the modifications viz., protonation, carboxylation and grafting with amine groups have been made. The modified forms viz., PCB, CCB and GCB were prepared as reported by Kousalya, Rajiv Gandhi, and Meenakshi (2010).

2.4. *Sorption experiments*

The batch adsorption experiments in duplicate were carried out. Sorption experiments were conducted in 250 mL reagent bottles containing 100 mL of various concentrations of Cu(II) solution using sorbent. The bottles were agitated at 200 rpm in a thermostatic shaking incubator to reach the equilibrium. The effect of contact time on the SC of sorbents was studied in the range 1–10 h at an initial copper concentration of 200 mg/L at pH 6. Effect of initial pH on the SC of sorbents for Cu(II) was studied by varying solution pH from 1 to 6 at the sorbent dosage of 0.1 g/100 mL for 5 h contact time using 200 mg/L initial copper concentration. The solution pH was adjusted with dilute HCl or NaOH solution. The effect of competitor common ions was studied using an initial concentration of 200 mg/L with the sorbent dosage of 0.1 g/100 mL for 5 h. Adsorption isotherms were studied at different initial copper concentrations viz., 50, 100, 150, 200 mg/L at different temperatures viz., 303, 313 and 323 K.

3. Results and discussion

3.1. *Characterization of modified chitosan beads*

FTIR spectrum of chitosan beads and modified chitosan beads are shown in Fig. 1. There is a possibility of overlapping between $-NH_2$ and –OH stretching vibrations, the strong broad band at the wavenumber region of 3300–3500 cm^{-1} is the characteristic of $-NH_2$ stretching vibration (Kousalya, Rajiv Gandhi, and Meenakshi, 2010). The major bands for the chitosan beads can be assigned as follows: 3440 cm^{-1}(–OH and $-NH_2$ stretching vibrations), 2921 cm^{-1} (–CH stretching vibration in –CH and $-CH_2$), 1652 cm^{-1} ($-NH_2$ bending vibration), 1379 cm^{-1}(–CH symmetric bending vibrations in –CHOH–), 1067 and 1028 cm^{-1}(–CO stretching vibration in –COH) (Li & Bai, 2005; Nalwa, 1997; Wade, 1999). After cross-linking the modified chitosan beads, the –OH and $-NH_2$ stretching vibration around the wavenumber of 3440 cm^{-1} and the $-NH_2$ bending vibration at the wavenumber 1652 cm^{-1} were shifted to lower frequencies.

Fig. 2 shows FTIR spectra of (a) GCB and (b) copper sorbed GCB. The interaction between Cu(II) and the sorbent is confirmed by the FTIR spectroscopy. After sorption, absorption band at 1650 and 1070 cm^{-1} corresponds to $-NH-CO-CH_3$ and C=O stretching band decrease, and the band at 1586 cm^{-1} for $-NH_2$ group disappears while the band at 1325 cm^{-1} corresponds to N–Cu–O group appears which indicates formation of complex between Cu(II) and GCB (Cheng, Liu, Han, & Ma, 2010; Kyzas, Kostoglou, & Lazaridis, 2009).

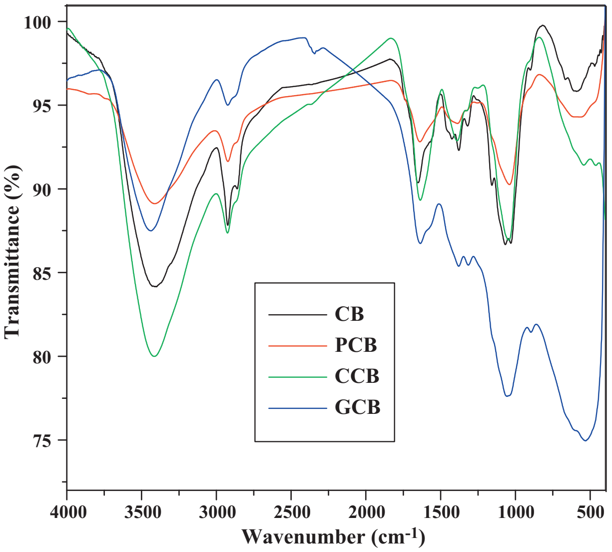

Fig. 1. FTIR spectra of CB, PCB, CCB and GCB.

The broad bands at about 3300–3570 cm^{-1} which are concerned with –OH and –NH stretching vibrations decrease after sorption process. This may be attributed to the deformation of O–H and N–H bands as a result of interaction between the functional groups and metal ions. In addition, the surface charge density gives an overall intensity of charges on the solid matrix surface. A transport study of chitosan indicates that copper is chelated with the $-NH_2$ and –OH groups in the chitosan (Findon, McKay, & Blair, 1993). It was also confirmed that the amino groups of chitosan are the major effective binding sites for metal ions, forming stable complexes by co-ordination (Chui, Mok, Ng, Luong, & Ma, 1996). The electrons present on nitrogen in the amino groups can establish a dative bond with transitional metal ions. Some hydroxyl groups in the chitosan may function as donors. Hence deprotonated hydroxyl groups involved in the co-ordination with Cu(II) (Lerivrey, Dubois, Decock, & Micera, 1986; Popuri, Vijaya, Boddu, & Abburi, 2009).

SEM images of GCB and copper-sorbed GCB are shown in Fig. 3. Fresh GCB has many pores on the surface of the beads (Fig. 3a). Fig. 3b shows that there is a mass transfer of copper ions onto the copper-sorbed GCB which results in reduction of pores indicates the copper sorption.

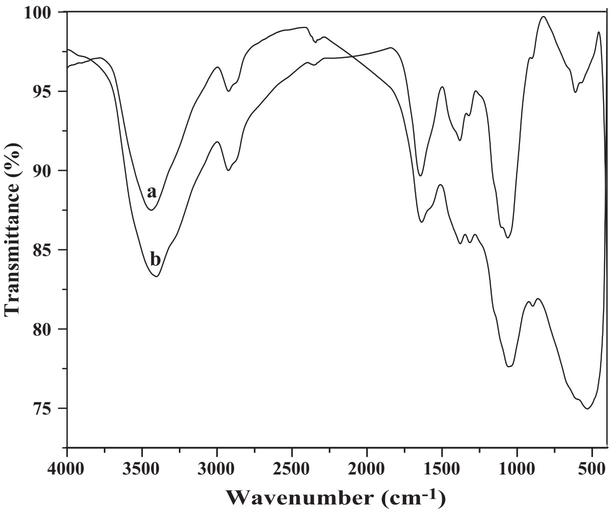

Fig. 2. FTIR spectra of (a) GCB and (b) copper sorbed GCB.

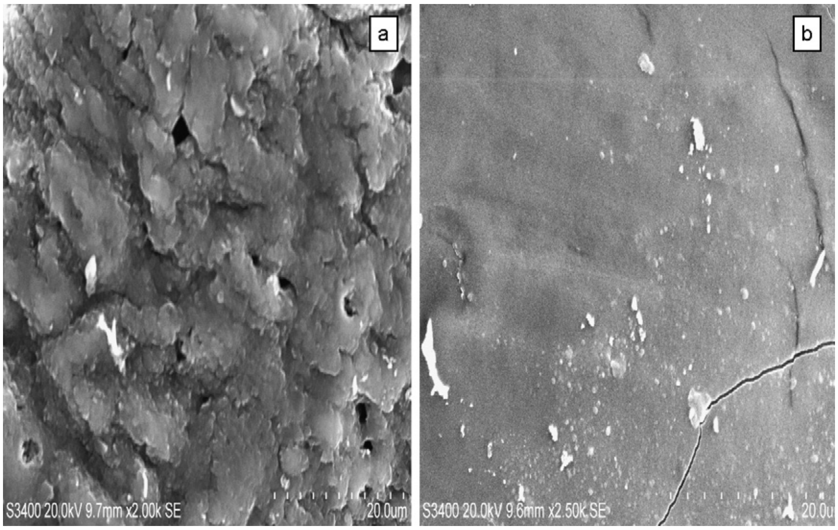

Fig. 3. SEM images of (a) GCB and (b) copper sorbed GCB.

3.2. *Effect of contact time*

The sorption capacity of CB, PCB, CCB and GCB were found out by varying contact time in the range of 1–10 h. About 0.1 g of the sorbent was placed into 100 mL of the 200 mg/L initial copper solution. It is clear from Fig. 4a that the SC of all the sorbents reached saturation after 5 h. As a result, 5 h was fixed as the contact time for all the sorbents for further studies. The maximum SC of CB, PCB, CCB, and GCB were found to be 40, 52, 86 and 126 mg/g respectively. Among the sorbents, GCB experienced higher SC than PCB and CCB which are in turn higher than CB.

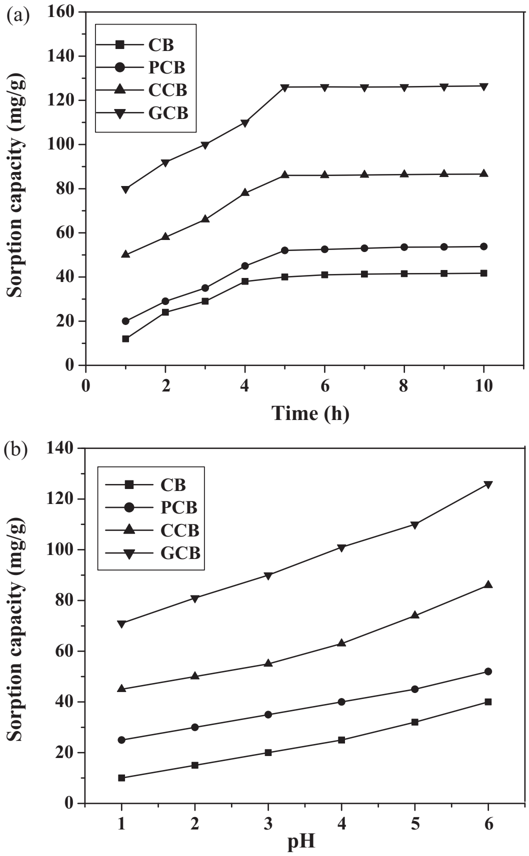

Fig. 4. (a) Effect of contact time on the SC of the sorbents at 303 K and (b) influence of pH on the SC of the sorbents at 303 K.

3.3. *Influence of pH*

The removal of copper from the aqueous solution was highly dependent on the solution pH (Kousalya, Rajiv Gandhi, Viswanathan, & Meenakshi, 2010). Hence the SC of all the sorbents was determined at different pH levels and the results are shown in Fig. 4b. It is apparent from Fig. 4b that the pH has influenced the SC of the sorbents. A maximum SC was observed at pH 6 and a slight decline in SC was observed in acidic medium. In acidic medium, SC of all the sorbents decreases due to the protonation of amine group, which reduces the number of binding sites for the sorption of Cu(II) and hence at this pH, removal of Cu(II) is governed by exchange. But the competition exerted by H^+ again retards Cu^{2+} exchange. As, the concentration of H^+ ions decreases with increasing pH of the medium, more number of Cu(II) get exchanged and hence observed a higher sorption near pH 6. At pH value higher than 6, the adsorption studies could not be carried out because of the precipitation of Cu(II) as $Cu(OH)_2$. As the modified chitosan beads possessed higher SC than the CB at all pH ranges studied, further studies were limited to modified chitosan beads and through out the study the pH of the medium was maintained at 6 without adjusting the solution pH.

3.4. *Effect of common ions in the medium*

The SC of the sorbents in the presence of other common ions which are normally present in water viz., Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^- ions were investigated with a fixed initial concentration of 500 mg/L of these ions by keeping 200 mg/L as initial copper concentration with the sorbent dosage of 0.1 g/100 mL for 5 h at 303 K. Effects of co-ions have a slight effect on SC. The SC was varied between 118 and 120 mg/L in the presence of common ion while it was 126 mg/L in the absence of common ion for the sorption of Cu(II). Parallel results were obtained for PCB and CCB. This may be attributed to the fact that the modified chitosan beads selectively remove copper even in the presence of other co-ions.

3.5. *Sorption isotherm models*

The two most commonly used isotherms namely Freundlich and Langmuir are used to describe the adsorption characteristics of modified chitosan beads.

Table 1
Freundlich and Langmuir isotherms of the modified chitosan beads on copper sorption.

Sorbents	Temp. (K)	Freundlic isotherm					Langmuir isotherm				
		$1/n$	n	k_F ((mg/g) (L/mg)$^{1/n}$)	r	χ^2	Q° (mg/g)	b (L/g)	R_L	r	χ^2
PCB	303	0.640	1.56	2.50	0.996	0.102	102.56	0.0090	0.847	0.993	0.138
	313	0.637	1.57	2.90	0.999	0.060	114.03	0.0094	0.841	0.995	0.069
	323	0.654	1.53	2.92	0.999	0.040	127.71	0.0088	0.850	0.997	0.238
CCB	303	0.650	1.54	2.83	0.996	0.036	130.72	0.0079	0.863	0.966	0.999
	313	0.668	1.50	3.03	0.995	0.079	137.55	0.0092	0.844	0.992	0.126
	323	0.672	1.49	3.45	0.966	0.508	141.64	0.0010	0.980	0.956	0.519
GCB	303	0.805	1.24	1.54	0.996	0.091	165.02	0.0062	0.889	0.987	4.693
	313	0.748	1.34	2.16	0.993	0.192	176.37	0.0061	0.891	0.977	4.809
	323	0.704	1.42	2.83	0.996	0.126	215.05	0.0059	0.894	0.992	10.360

3.5.1. *Freundlich isotherm*

The linear form of Freundlich (1906) isotherm is represented by the equation:

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e \tag{1}$$

where q_e is the amount of copper adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of copper in solution (mg/L), k_F, a measure of adsorption capacity, and $1/n$, the adsorption intensity, were calculated from the slope and intercept of the plot $\log q_e$ vs. $\log C_e$ and the values are listed in Table 1. Freundlich isotherm constants for PCB, CCB and GCB were calculated from the linear plot of $\log q_e$ vs. $\log C_e$ and the values are presented in Table 1. The values of $1/n$ lying between 0 and 1 confirm the favorable conditions for adsorption. The k_F values for all the sorbents were found to increase with increase in temperature like SC increases with an increase in temperature confirm the endothermic nature of sorption. The r values for the modified sorbents are high indicating the applicability of Freundlich isotherm.

3.5.2. *Langmuir isotherm*

Langmuir (1916) isotherm model can be represented in the form of equation:

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \tag{2}$$

where Q° is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of sorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption calculated from the slope and intercept of the plot C_e/q_e vs. C_e and the values are shown in Table 1. The values of Q° for all the sorbents found to increase with an increase in temperature like SC once again confirms the endothermic nature and temperature dependence of the sorption process.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter R_L (Weber & Chakravorti, 1974).

$$R_L = \frac{1}{1 + bC_o} \tag{3}$$

The R_L values at different temperatures studied were calculated and are listed in Table 1. The R_L values lying between 0 and 1 indicated that the conditions were favorable for adsorption. The higher r values of Freundlich over Langmuir isotherm indicated the suitability of Freundlich isotherm than the Langmuir isotherm.

3.5.3. *Chi-square analysis*

To identify the suitable isotherm for sorption of copper onto modified chitosan beads, chi-square analysis was carried out. The mathematical statement for chi-square (Ho, 2004) analysis is:

$$\chi^2 = \sum \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \tag{4}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data on the equilibrium capacity (mg/g). The values of χ^2 are presented in Table 1. The low chi-square values of Freundlich isotherm than Langmuir isotherm for all the sorbents taken for the investigation indicates the applicability of Freundlich isotherm.

3.6. *Thermodynamic treatment of the sorption process*

The effect of temperature is a major influencing factor in the sorption process. The copper sorption onto modified chitosan beads was monitored at three different temperatures viz., 303, 313 and 323 K under the optimized conditions and thermodynamic parameters like standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated as follows, The change in free energy of sorption is given by:

$$\Delta G^0 = -RT \ln K_0 \tag{5}$$

where K_o is the sorption distribution coefficient, ΔG° is the free energy of sorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The sorption distribution coefficient K_o was determined from the slope of the plot $\ln(q_e/C_e)$ against C_e at different temperatures and extrapolating to zero C_e according to Khan and Singh (1987) method.

The sorption distribution coefficient can be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature:

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

where ΔH° is the standard enthalpy change (kJ/mol) and ΔS° is the standard entropy change (kJ/(mol K)). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K_o$ against $1/T$.

Table 2
Thermodynamic parameters of the modified chitosan beads on the removal of copper.

Thermodynamic parameters		PCB	CCB	GCB
ΔG° (kJ mol^{-1})	303 K	−13.28	−13.30	−14.04
	313 K	−13.56	−13.64	−14.19
	323 K	−14.04	−14.12	−14.23
ΔH° (kJ mol^{-1})		1.736	0.813	11.148
ΔS° (kJ mol^{-1} K^{-1})		0.038	0.041	0.012

Table 3
Maximum adsorption capacity (mg/g) of different chitosan based adsorbents for Cu(II).

Adsorbents	Maximum adsorption capacity (mg/g)	References
Grafted chitosan beads	126.0	Present study
Carboxlated chitosan beads	86.0	Present study
Protonated chitosan beads	52.0	Present study
Chitosan	16.8	Huang, Chung, and Ming (1996)
Chitosan	33.4	Wan Ngah, Kamari, and Koav (2004)
Chitosan/PVA	47.9	Wan Ngah et al. (2004)
Chitosan acetate crown ether	23.9	Tan, Wang, Peng, and Tang (1999)
Chitosan diacetate crown ether	31.3	Tan et al. (1999)
Epichlorohydrine cross-linked chitosan	16.8	Tan et al. (1999)
Chitosan-coated PVC	87.9	Popuri et al. (2009)
Pristine chitosan	13.3	Saiano, Ciofalo, Cacciola, and Ramirez (2005)
Chitosan/cellulose composite	53.3	Liu and Bai (2006)
Epichlorohydrine chitosan	62.2	Wan Ngah, Endud, et al. (2002)
Glutaraldehyde-chitosan	59.6	Wan Ngah, Endud, et al. (2002)
Ethylene glycol diglycidyl ether crosslinked chitosan	45.7	Wan Ngah, Endud, et al. (2002)
Epichlorohydrine cross-linked chitosan	39.3	Coelho et al. (2007)
Chitosan modified with reactive blue 2	57.1	Vasconcelos, Favere, Goncalves, and Laranjeira (2007)
N-(4-pyridylmethyl) chitosan	45.1	Rodrigues, Laranjeira, de Favere, and Stadler (1998)
Chitosan modified with N–N′-[bis(2-hydroxy-3-formyl-5-methylbenzyldimethyl)]-ethylenediamine	113.6	Vasconcelos et al. (2008)
Chitosan crosslinked with epichlorohydrine	35.4	Chen et al. (2008)
Glutaraldehyde-crosslinked metal-complexed chitosans	33.0	Chen, Yang, Chen, Chen, and Chen (2009)
Chitosan modified with sulphoxine chelant agent	53.8	Vitali, Laranjeira, Fávere, and Goncalves (2008)
Chitosan modified with Reactive Orange 16 dye	107.3	Vasconcelos, Guibal, Laus, Vitali, and Fávere (2009)
Chitosan modified with N–N′-[bis(2-hydroxyl-3-formyl-5-methylbenzyl-dimethyl)]-ethylenediamine	109.0	Justi, Fávere, Laranjeira, Neves, and Peralta (2005)
Chitosan-tripolyphosphate	26.0	Wan Ngah and Fatinathan (2010)
Modified chitosan transparent thin membrane	8.4	Cheng et al. (2010)
Chitosan-coated sand	8.1	Wan, Kan, Rogel, and Dalida (2010)
Chitosan-glutaraldehyde 1:1	31.2	Wan Ngah and Fatinathan (2008)
Chitosan-glutaraldehyde 2:1	19.5	Wan Ngah and Fatinathan (2008)
Chitosan-alginate beads	67.6	Wan Ngah and Fatinathan (2008)
Crosslinked magnetic chitosan beads	78.1	Guolin, Chuo, Kai, and Jeffrey (2009)
Chitosan/cellulose acetate blend hollow fiber membranes	48.2	Liu and Bai (2006)
Epichlorohydrin crosslinked xanthate chitosan	43.4	Kannamba, Laxma Reddy, and AppaRao (2010)
Chitosan	17.7	Ilauro and Claudio (2004)
Chitosan-coated alumina	86.2	Boddu, Abburi, Randolph, and Smith (2008)
Crab shell	19.8	Dahiya, Tripathi, and Hegde (2008)
Arca shell	18.3	Dahiya et al. (2008)
Alginate/phosphorylated chitin blend film	11.7	Jayakumar, Rajkumar, Freitas, Selvamurugan, et al. (2009)
Chitosan-bound Fe_3O_4 magnetic nanoparticles	21.3	Chang and Chen (2005)
Chitosan powder	45.0	Huang, Liou, Liu, and Huang (1994)
Chitosan flakes	20.9	Bassi, Prasher, and Simpson (2000)
Prawn shell	17.1	Chu (2002)
Chitosan-coated magnetic nanoparticles modified with α-ketoglutaric acid	96.1	Zhou, Nie, White, He, and Zhu (2009)
Carboxymethyl chitosan-*graft*-D-glucuronic acid membranes	70.2	Jayakumar, Rajkumar, Freitas, Sudheesh Kumar, et al. (2009)
Thiourea-modified magnetic chitosan microspheres	66.7	Zhang, Wang, Liu, Huang (2009)
Chitosan	1.5	Silva et al. (2008)

The calculated values of the thermodynamic parameters of PCB, CCB and GCB are shown in Table 2. The negative values of ΔG° confirm the spontaneous nature of copper sorption. The positive value of ΔS° indicates that the freedom of Cu(II) ions is not too restricted in the sorbents. The positive value of ΔH° for copper removal confirms the endothermic nature of sorption process.

3.7. *Mechanism of copper sorption*

The mechanism of removal of copper by the modified chitosan beads was governed by adsorption, ion-exchange and chelation. The lone pair of electrons present in O and N of the respective hydroxyl and amino groups present in the chitosan beads chelates Cu(II). PCB remove copper by ion-exchange mechanism while CCB removes by means of both ion-exchange as well as chelation as it contains the exchangeable hydrogen ions and metal chelating amino groups. In the case of GCB, the number of chelating amino groups has been increased through grafting which provides more active sites for chelating copper and hence experienced a higher SC than CCB which in turn was higher than PCB.

A comparison of the SC of the chitosan based adsorbents reported in the literature for Cu(II) removal from aqueous solution relative to the behaviour of modified chitosan beads is presented in Table 3. Modified chitosan beads possess an enhanced sorption capacity which confirms their selectivity towards Cu(II).

4. Conclusions

Among the modified forms of chitosan, GCB showed higher SC towards Cu(II) than CCB, PCB and CB. The pH of the medium has an influence on the sorption of Cu(II) onto modified chitosan beads and a maximum SC was observed at pH 6. Modified forms of chitosan removes Cu(II) selectively in the presence of common ions present in water. The sorption data follows Freundlich isotherm. The nature of sorption process is spontaneous and endothermic. The mechanism of copper sorption onto all the modified forms of chitosan beads is governed by adsorption, ion-exchange and chelation.

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