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Synthesis and characterization of a crosslinked chitosan derivative with a complexing agent and its adsorption studies toward metal(II) ions

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ABSTRACT

A new chitosan derivative has been synthesized by crosslinking a metal complexing agent, [6,6′-piperazine-1,4-diyldimethylenebis (4-methyl-2-formyl) phenol] (L), with chitosan (CTS). The resulting material (CCTSL) was characterized by elemental (CHN), spectral (FTIR and solid-state NMR), thermal (TGA and DTA), and structural (powder XRD and SEM) analyses. Adsorption experiments (pH dependency, kinetics, and equilibrium) of CCTSL toward various metal ions such as Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II) were carried out at 25 °C. The results showed that the adsorption was dependent on the pH of the solution, with a maximum capacity between pHs 6.5 and 8.5. The kinetics was evaluated by applying the pseudo-first-order and pseudo-second-order equation models and the equilibrium data were analyzed by Langmuir isotherm model. The maximum adsorption capacity was 1.21 mmol g^{-1} for Cu(II) and the order of adsorption capacities for the metal(II) ions studied was found to be Cu(II) > Ni(II) > Cd(II) $\geqslant$ Co(II) $\geqslant$ Mn(II) $\geqslant$ Fe(II) $\geqslant$ Pb(II).

1. Introduction

Contamination of aquatic media by heavy metal ions is a serious environmental problem, mainly due to the discarding of industrial wastes.[1,2] Heavy metals are highly toxic even at low concentrations and can accumulate in living organisms, causing several disorders and diseases.[3–5] Metals can be distinguished from other toxic pollutants, since they undergo chemical transformations, are non-biodegradable, and have great environmental, economic, and public health impacts.[6,7] The chitosan (CTS) biopolymer has proved to be an effective transition metal ion adsorber. Chitin/chitosans, which are unique even among polysaccharides, contain amino groups as constituent carbohydrate units, so that their use in conjunction with chemical crosslinking agents such as isocyanates, aldehydes, and carbodiimides in wound dressings, anti-adhesion materials, and metal ion absorbents has been studied.[8–11] The insertion of crosslinking agent with functional groups in the chitosan matrix may improve its capacity of interaction with metal ions by complexation.

The studies on crosslinked chitosan derivative that has a metal ion complexing agent as a crosslinker are sparse.[12] Thus, the present invention offers a functional chitosan derivative incorporating at least a portion of the 2-position amino groups in the glucosamine units forming Schiff base derivative with [6,6′-piperazine-1,4-diyldimethylenebis (4-methyl-2-formyl) phenol]. The new crosslinked chitosan ligand (CCTSL) was characterized by elemental analysis, FT-IR, ^{13}C NMR, and SEM studies. The adsorbent capacity of this new polymer with various metal ions such as Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II) was studied.

2. Experimental

2.1. Materials

Chitosan of a low molecular weight was purchased from Aldrich (Cat. Number 44,8869) with a deacetylation percentage in the range of 75–85% with Brookfield viscosity 20 cps, and was used as received. [6,6′-piperazine-1,4-diyldimethylenebis (4-methyl-2-formyl) phenol] was used as the crosslinking agent and was prepared by following the literature procedure.[13]

Stock solutions (1000 mg L^{-1}) of Mn(II), Fe(II), Co(II), Cu(II), and Ni(II), were prepared by dissolving the appropriate amount of metal(II) sulfate (analytical grade) in double distilled water and were standardized with a standard solution of 0.01 mol L^{-1} EDTA.[14] Whereas stock solutions (1000 mg L^{-1}) of Cd(II) and Pb(II) were prepared by dissolving the appropriate amount of their metal(II) nitrates (analytical grade) in double distilled water and their concentrations were estimated using the Atomic Absorption Spectrometry (AAS). Working standard solutions of all the metal ions were prepared through the dilution of the respective 1000 mg L^{-1} stock solutions with distilled water. All other chemicals and solvents were of analytical grade and were used as received.

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2.2. Synthesis of crosslinked chitosan derivative (CCTSL)

CCTSL was prepared by dissolving 1.0 g of chitosan powder (0.0048 mol of glucosamine residue) in 25 mL of 1 wt % acetic acid, diluted with methanol (150 mL) and then by reacting with 0.92 g of the crosslinking agent [6,6′-piperazine-1,4-diyldimethylenebis (4-methyl-2-formyl) phenol], (0.0024 mol) dissolved in methanol (20 mL). The mixture was stirred at room temperature for 16 h, followed by refluxing for 18 h, which resulted in a yellow-colored gel. It was then decanted and thoroughly washed with methanol to remove any unreacted crosslinking agent and then dried in vacuum at 60 °C to give CCTSL as a yellow-colored powder. Yield: 1.63 g (85%). *Analytical data for* CCTSL ($C_{34}H_{44}N_4O_{10}$). Found: C, 53.29; H, 6.25; N, 5.45.

2.3. Preparation of metal-CCTSL

The metal complexes of CCTSL were prepared by placing 50.0 mL of 100 mg L^{-1} of metal ion solutions buffered at pH 7.5 in contact with 50-mg sample of crosslinked chitosan (CCTSL) for a period of 4 h by shaking. After 4 h the shaking was turned off, and immediately thereafter the adsorbent material was decanted and dried at 60 °C.

2.4. Measurements

An elemental analysis was carried out on a Carlo Erba model 1106 elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer RX1 model spectrophotometer on KBr discs in the wavenumber range of 4000–250 cm^{-1}. TG and DTG analyses were carried out using TG-50 Shimadzu Model Thermogravimetric analyzer with a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere. Powder X-ray diffraction studies were carried out using a scientific high-resolution Guinier X-ray Powder diffractometer using Cu Kα1 radiation with a quartz monochromator. Micrographs of CCTSL before and after metal(II) ion adsorption were taken by using a JSM-5600LV, JEOL model scanning electron microscope. The metal(II) ion concentration was measured by using a Perkin Elmer AAnalyst-750 Model atomic absorption spectrophotometer (AAS).

2.5. Adsorption experiments

The metal ion adsorption properties of CCTSL and the effect of the pH on adsorption were studied from pH 3 to pH 10 utilizing various buffer solutions (KCl/HCl for pHs 2 and 3; acetic acid/sodium acetate for pHs 4, 5, and 6; tris(hydroxymethyl) aminomethane/HCl for pHs 7.5 and 8.5; and ammonia/ammonium chloride for pHs 9.5 and 10). Aliquots (50.0 mL) of 100 mg L^{-1} of metal ion solutions buffered at different pH values were placed in contact with 50-mg samples of modified chitosan (CCTSL) for a period of 4 h by shaking. After 4 h the shaking was turned off, and immediately thereafter the adsorbent material was decanted, and 2 mL of the filtrate was removed and diluted in volumetric flasks to determine the metal ion concentration by atomic absorption spectrophotometry (AAS). Each run was duplicated under identical conditions. The quantity of metal ion adsorbed at different pH values was calculated as follows:[15]

$$Q_e = \frac{(C_0 - C_e)V}{W},$$

where Q_e is the equilibrium adsorption capacity of the chitosan derivative (mg g^{-1} adsorbent), V is the volume of the solution (mL), C_0 and C_e are the initial and equilibrium concentrations of the solute, respectively, and W is the weight of the sorbent (g).

The amount of the metal ions adsorbed by the adsorbent can also be calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{WM},$$

where q_e is the adsorption capacity of the adsorbent at equilibrium (mmol g^{-1} adsorbent) and M is the atomic weight of the corresponding metal ion.

The adsorption kinetics was determined in a closed flask containing 50 mg of CCTSL and 50.0 mL of a metal ion solution buffered at pH 8.5. After pre-determined time periods, 2-mL aliquots were removed and the concentration of metal ion in the solutions was measured. It was observed that the adsorption process was fast, and reached equilibrium after 3 h and remained constant for 24 h.

3. Results and discussion

3.1. Synthesis and characterization of CCTSL

A new chitosan derivative CCTSL was obtained by crosslinking two equivalents of chitosan with one equivalent of crosslinking agent as shown in Scheme 1. The compound [6,6′-piperazine-1,4-diyldimethylenebis (4-methyl-2-formyl) phenol] introduces new complexing groups into the chitosan, such as phenolic and piperazine groups, conferring metal ion chelation properties on the new adsorbent. Concurrently, the reaction between aldehyde groups from the complexing agent and amine groups from chitosan results in Schiff base formation leading to crosslinking in the polymeric structure. This new adsorbent has a special characteristic, that is, it does not require the use of additional crosslinking agents, such as glutaraldehyde whereas the complexing agent itself acts as a crosslinking agent.

The new adsorbent material was characterized by spectral, thermal, and powder X-ray diffraction (XRD) studies. The surface modification of the material was analyzed using a scanning electron microscope (SEM).

An elemental analysis showed the *C/N* ratios to be 6.05 and 9.77 for the CTS and CCTSL, respectively. From this, we infer that the functional group attached to the chitosan was around 60%.

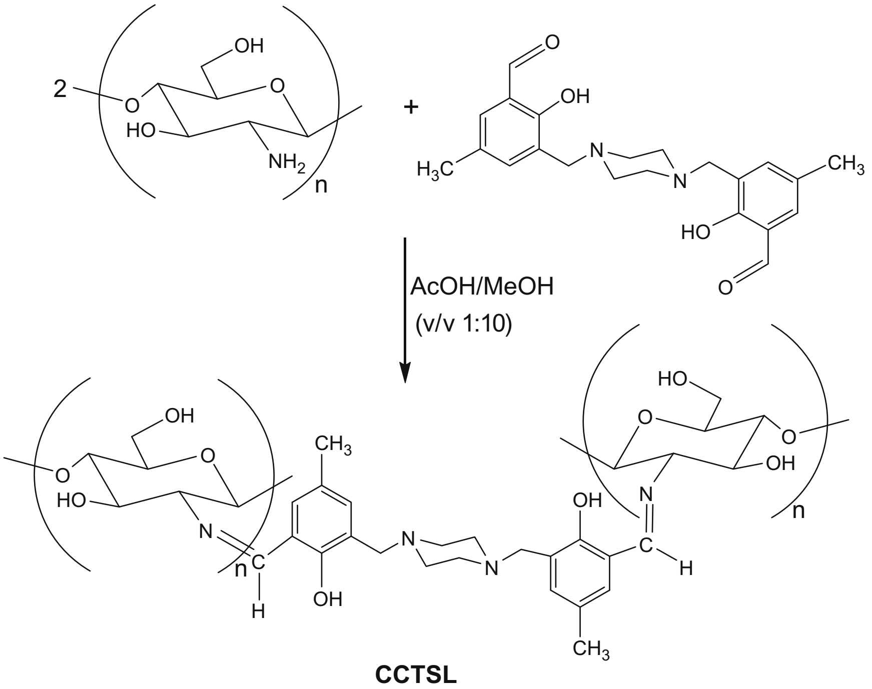
The degree of substitution (DS) of the crosslinker to $-NH_2$ groups on chitosan was calculated using the following equation:[16,17]

$$\mathrm{DS} = \frac{a(C/N)_m - (C/N)_o}{n}$$

where $(C/N)_m$ is the *C/N* of the modified chitosan derivative, $(C/N)_o$ is the *C/N* of the original chitosan, and *a* and *n* are the number of nitrogens and carbons introduced after chitosan modification, respectively. The DS obtained for CCTSL is 0.61.

The IR spectra of CCTSL exhibit additional peaks around 3420 cm^{-1} for phenolic –OH group and between 1610 and 1650 cm^{-1} for imine (–C=N) group apart from that of free chitosan.[17] Further, peaks around 1400–1500 cm^{-1} are due to aromatic backbone vibration and the peak around 1250–1265 cm^{-1} is due to the phenolic C–O group of the crosslinker moiety.[18–21] The ^{13}C NMR spectrum of CCTSL is shown in Figure 1. When the ^{13}C NMR spectra of CCTSL were compared with those of the chitosan, additional peaks were observed in the region 120–180 ppm which were attributed to the aromatic carbon atoms present in the chitosan derivative. The difference in the nature and intensity of the peaks in the region 20–110 ppm of CCTSL when compared to chitosan indicates that the additional aliphatic carbon atoms are present in these derivatives.[22,23]

The TG–DTG curve of CCTSL is shown in Figure 2. The thermal degradation study of the CCTSL exhibits thermal decomposition of the polymer in the range 200–400 °C which takes place at a tem-



Scheme 1. Synthesis of CCTSL.

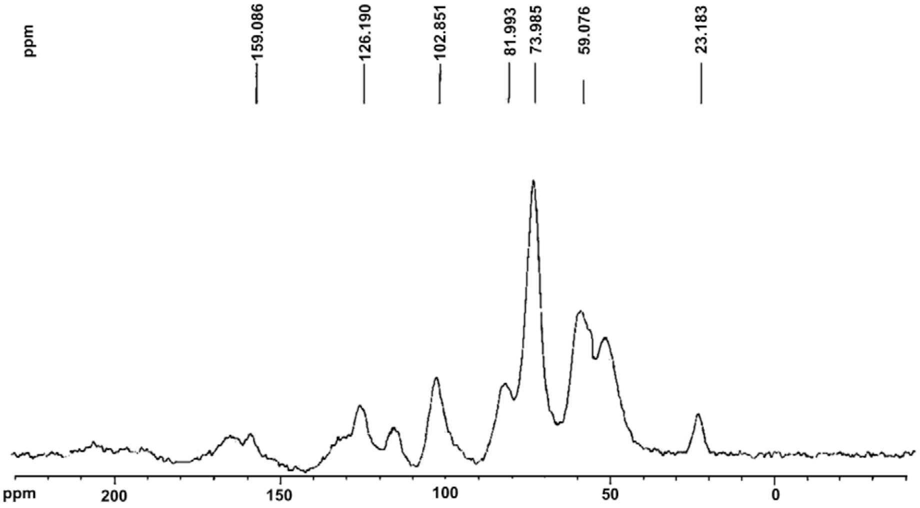


Figure 1. Solid-state ^{13}C NMR spectrum of CCTSL.

perature that is lower than that at which the secondary degradation of chitosan occurs indicating that CCTSL is less stable than chitosan. It seems that the low stability of this material when compared to chitosan may be due to a decrease in the number of primary amino groups after chemical modification process.[18] Powder X-ray diffraction patterns of CCTSL were compared with those of chitosan.[24] Free chitosan shows the characteristic peak at $2\theta = 10$ °C, due to the presence of (0 0 1) and (1 0 0), and that at $2\theta = 20$ °C caused by the presence of (1 0 1) and (0 0 2). For CCTSL, the intensity of peaks at $2\theta = 10$ °C and 20 °C decreased and the peaks were broadened more than those of free chitosan. It was thought that the decrease in the crystallinity of the chitosan derivative could be attributed to the deformation of the strong hydrogen bond in the free chitosan molecule, and also due to the bulkier complexing agent substitution onto it. This low crystallinity indicates that it was considerably more amorphous than free chitosan.[18,25] The difference in structural morphology between the chitosan and CCTSL copolymer has also been further supported by the difference in their SEM images (Fig. 3). A micrograph of CCTSL displayed a more extensive three-dimensional network compared with the smooth lacunose surface of chitosan[26] which is attributed to the immobilization of complexing agent on the polymer surface.

3.2. Characterization of metal-CCTSL

The metal complexes of CCTSL were prepared by the adsorption of one mole of metal(II) ions such as Mn(II), Fe(II), Co(II),

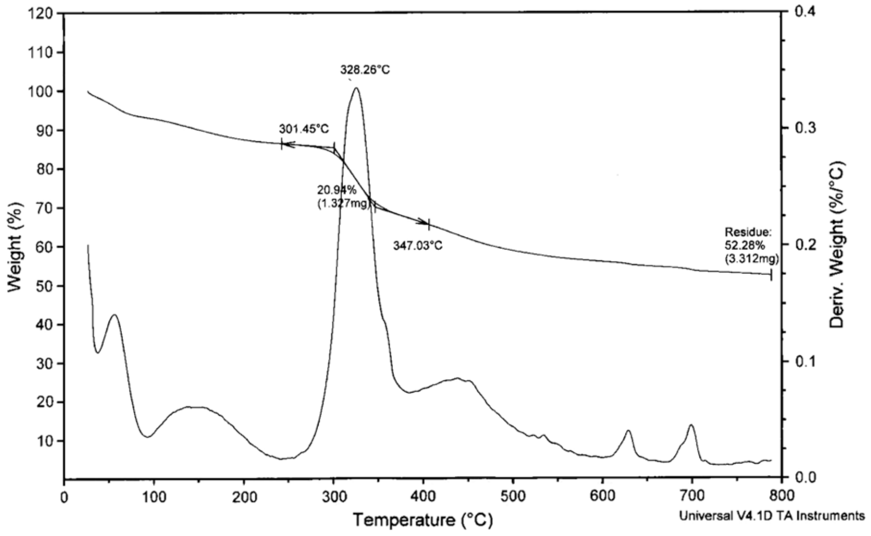


Figure 2. TG–DTG curve of CCTSL.

Cu(II), Ni(II), Cd(II), Pb(II), and Hg(II) on equimolar chitosan derivative in an aqueous solution (pH 7.5). The resulting M-CCTSL was characterized using IR spectral analysis and SEM analysis. The IR spectra of Cu-CCTSL showed new adsorption bands at 520 and 472 cm^{-1}, which may be due to the stretching vibration of N–Cu and O–Cu, respectively. When the SEM images of the complexed Cu-CCTSL and Mn-CCTSL (Fig. 3) were compared to that of CCTSL, a surface of the metal-complexed derivative that exhibited more pores was observed which may be due to the metal sites coordinated to chitosan derivative.[16,26] The proposed struc-

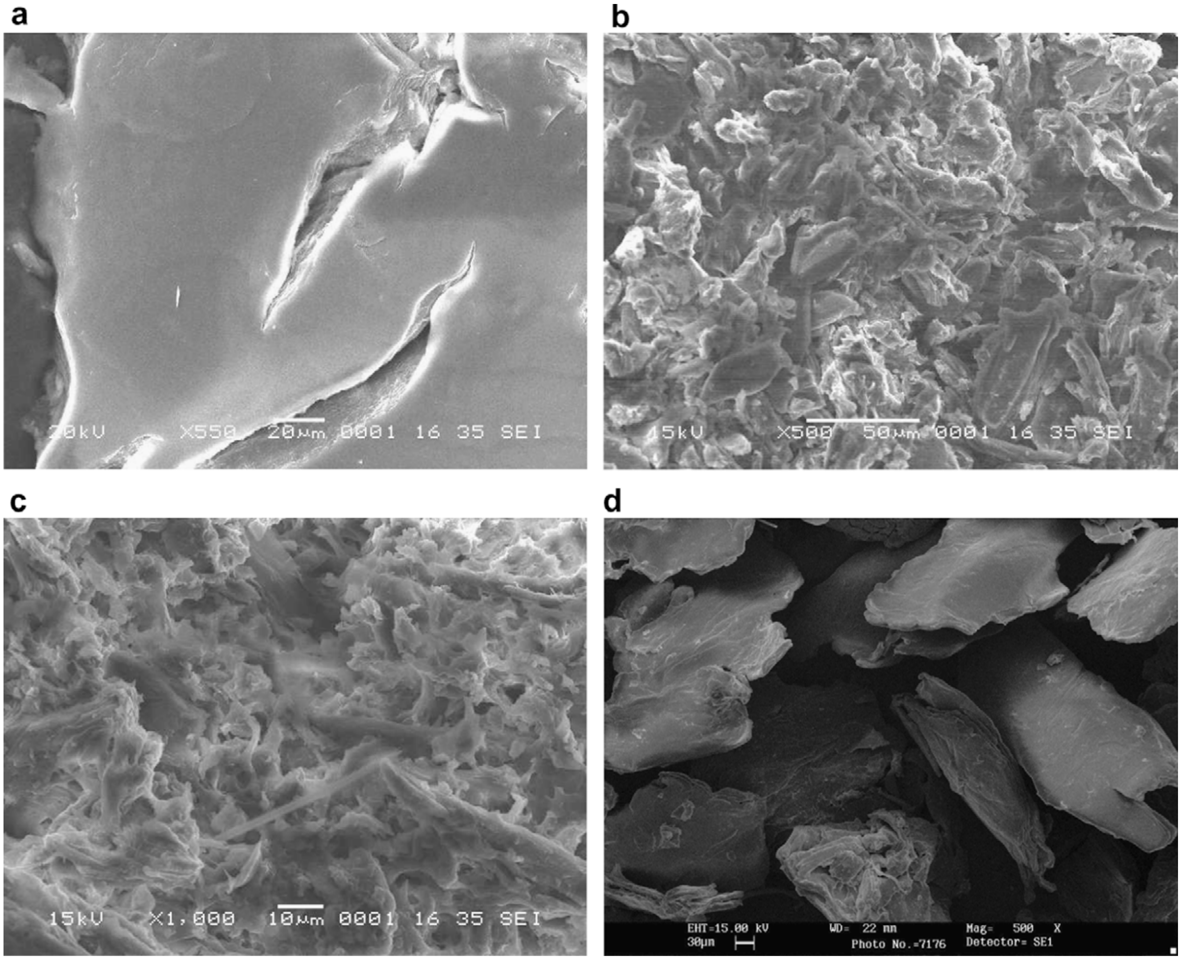


Figure 3. SEM images of (a) CTS; (b)CCTSL; (c) Cu-CCTSL; and (d) Mn-CCTSL.

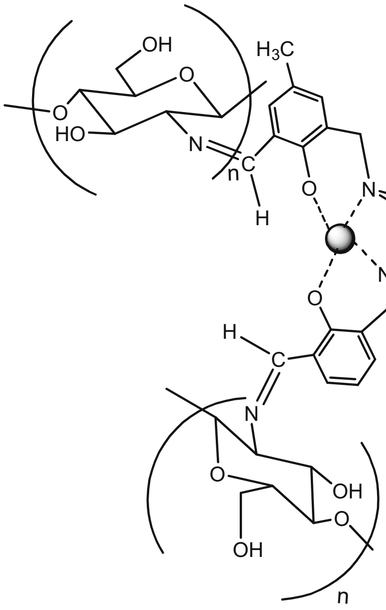


Figure 4. Metal-CCTSL.

ture for the metal-complexed chitosan derivative CCTSL is shown in Figure 4.

3.3. Adsorption studies

3.3.1. Effect of pH on adsorption

The effect of pH on the adsorption of metal ions of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) by crosslinked chitosan derivative CCTSL is illustrated in Figure 5. From this study, we infer that the adsorption capacity of mononucleating chitosan derivative is affected by the pH.[25–28] The metal(II) ion adsorption by CCTSL increases with the pH of the solution from 3.5 to maximum values of 6.5–8.5 and then decreases when pH increases beyond 8.5. At acidic pHs 3.5–5.5, the lower adsorption of the metal ions is attributed to the protonation of the complexation site (amine), which decreases the complex formation by the crosslinked chitosan derivative with metal ion.[19] Around pHs 6.5–8.5 the amino group exists as a free amine (without protonation) and in addition, the deprotonation takes place at the phenolic group present in the chitosan derivative which increases the metal ion uptake by the adsorbent. Whereas at pH above 8.5, the auxiliary complexation agents from buffer solutions can form complexes with the metal ion in order to avoid precipitation of the metal hydroxide which lowers the adsorption of the metal ion by the chitosan derivative. It is also observed that the solutions containing Fe(II) and Mn(II) become opaque at pH values above 8.5. The results also indicate that CCTSL has a good adsorption capacity for Cu(II), in the pH ranges studied, suggesting possible selectivity for this metal. The adsorption capacities of the crosslinked chitosan derivative CCTSL toward metal(II) ions studied in the present work are given in Table 1.

The adsorption capacities of the crosslinked chitosan derivative (CCTSL) toward various metal ions are higher than those of the free chitosan and are comparable to those of other chitosan derivatives reported in the literature.[15,29–31] From the studies, we infer that the order of metal adsorption capacities in mmol g^{-1} for these derivatives is Cu(II) > Ni(II) > Cd(II) ⩾ Co(II) ⩾ Mn(II) ⩾ Fe(II) ⩾ Pb(II). The crosslinked chitosan derivative also has a higher adsorption capacity toward Cu(II) ions. From this, we infer that this derivative has better selectivity toward Cu(II) ion than the other metal ions studied.

3.3.2. Adsorption kinetics

The adsorption kinetic behavior of crosslinked chitosan derivative CCTSL toward Cu(II) ions is illustrated in Figure 6 and the kinetic curve for Cu(II) showed that the adsorption was rapid in the first few minutes, reached equilibrium after approximately 90 min, and remained constant for 24 h. The kinetic parameters for adsorption of Cu(II) by CCTSL at pH 6.5 are given in Table 2.

The second-order rate constant obtained for CCTSL is 1.3×10^{-3} g mg^{-1} min^{-1} and Q_e cal of 60.9 mg g^{-1} toward Cu(II) ions in solution with $R = 0.999$ was best fit when compared to the first-order rate constant of 2.1×10^{-2} min^{-1} and 31.6 mg g^{-1} with $R = 0.934$ where Q_e was experimentally found to be 59.2 mg g^{-1} evidencing that chemical sorption is the rate-limiting step of adsorption mechanism.[32]

Table 1
Adsorption capacities of CCTSL at pH 8.5

Metal(II) ion	Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(II)	Cd(II)	Pb(II)
Q_e (mg g^{-1})	76.88	38.15	27.11	23.62	23.45	58.45	84.95
q_e (mmol g^{-1})	1.21	0.65	0.46	0.43	0.42	0.52	0.41

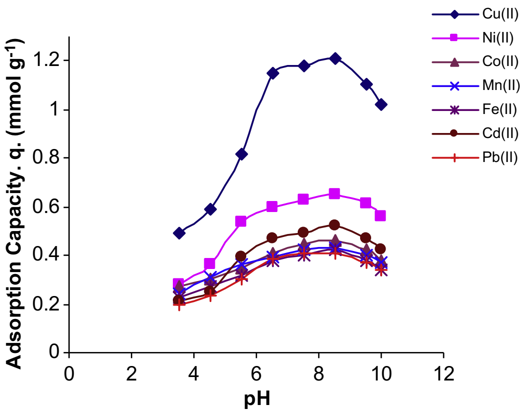


Figure 5. Effect of pH on metal(II) ion adsorption by CCTSL. {[M^{2+}] = 100 mg L^{-1}; temperature = 25 °C; contact time = 2 h; shaking rate = 200 rpm; and adsorbent mass = 50 mg}.

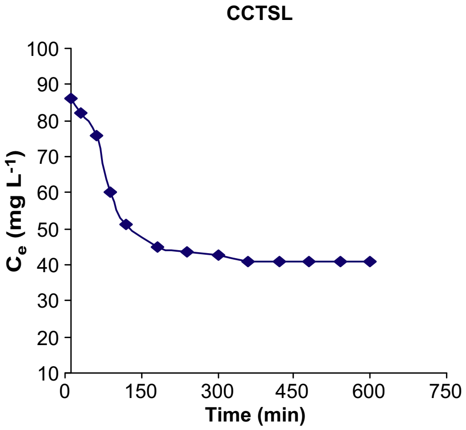


Figure 6. Kinetics on adsorption of Cu(II) by CCTSL. {[M^{2+}] = 100 mg L^{-1}; pH 8.5; temperature = 25 °C; contact time = 2 h; shaking rate = 200 rpm; and adsorbent mass = 50 mg}.

Table 2
The rate constants of crosslinked chitosan derivative CCTSL toward Cu(II) ions

Compound	Q_e, exp (mg g^{-1})	Rate constant					
		First-order			Second-order		
		k_1 (min^{-1})	Q_e, cal (mg g^{-1})	R	k_2 (g mg^{-1} min^{-1})	Q_e, cal (mg g^{-1})	R
Cu-CCTSL	59.2	2.1×10^{-2}	31.6	0.934	1.3×10^{-3}	60.9	0.999

3.3.3. Adsorption isotherms

The equilibrium studies were carried out for CCTSL toward various metal(II) ions at the pH value of optimum adsorption (pH 8.5) and with the necessary contact time to reach the adsorption equilibrium of each metal. The adsorption equilibrium isotherms for CCTSL are illustrated in Figure 7.

The linearization according to the Langmuir model of adsorption isotherms for various metal(II) ions by CCTSL is shown in Figure 8. The results obtained from the adsorption isotherms according to the Langmuir model are given in Table 3.

The linearizations according to the Langmuir model of adsorption isotherms for various metal(II) ions by CCTSL show good correlation coefficients (R >0.99) with the experimental data from adsorption equilibrium of metal ions suggesting homogeneous adsorption, which means a monolayer. The maximum adsorption capacity (q_m) obtained for Cu(II) was higher than the values found for other metal ions showing the following capacity order:Cu(II) > Ni(II) > Cd(II) ⩾ Co(II) ⩾ Mn(II) ⩾ Fe(II) ⩾ Pb(II).

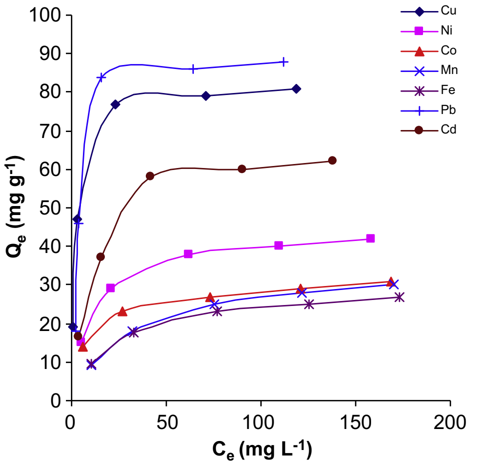


Figure 7. Adsorption equilibrium isotherms by CCTSL. {Temperature = 25 °C; contact time = 1 h; and adsorbent mass = 50 mg}.

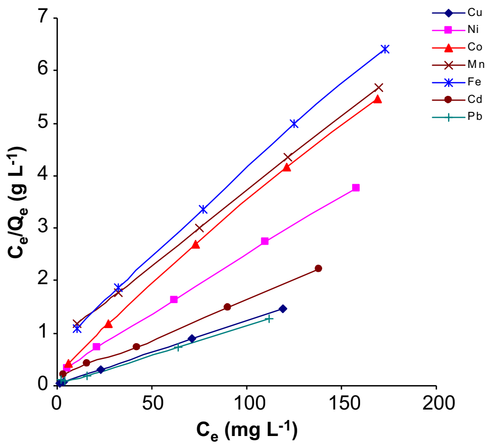


Figure 8. Linearization according to Langmuir model of adsorption isotherms by CCTSL.

Table 3
Parameters for various metal(II) ion adsorption by CCTSL according to Langmuir isotherm model

Metal(II) ion	Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(II)	Cd(II)	Pb(II)
K_L (L mg^{-1}) × 10^{-2}	38.7	9.3	9.2	7.4	3.2	6.0	21.3
Q_m, cal (mg g^{-1})	82.64	44.44	32.36	44.25	35.34	61.11	91.74

This datum is in agreement with the study carried out by Justi et al.[32] and Vold et al.,[33] where chitosan adsorbed Cu(II) selectively in the presence of other metal ions studied. The adsorption capacities of a chitosan that was not crosslinked for Cu(II), which was obtained by Huang et al.[34] and Justi et al.[32] in a powder form, were 45.2 mg g^{-1} and 54.3 mg g^{-1}, respectively; these values are lower than the ones obtained from this study. Therefore, chemical modification on chitosan improved the adsorption capacity for copper ions on the crosslinked form of the polymer.

4. Conclusion

A new crosslinked chitosan derivative (CCTSL) has been synthesized and characterized. The adsorption capacities of this derivative toward various metal ions are higher than those of the other crosslinked chitosan derivatives reported in the literature. This may be due to the additional coordination sites available in the crosslinker for metal ions. Among the metal ions studied, the CCTSL showed a higher adsorption capacity for copper(II) metal ions in aqueous solution.

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References

1. Baraka, A.; Hall, P. J.; Heslop, M. J. *J. Hazard. Mater.* **2007**, *140*, 86–94.
2. Bose, P.; Bose, M. A.; Kumar, S. *Adv. Environ. Res.* **2002**, *7*, 179–195.
3. Crini, G. *Bioresour. Technol.* **2006**, *60*, 67–75.
4. Aksu, Z. *Process Biochem.* **2005**, *40*, 997–1026.
5. Forgacs, E.; Cserhati, T.; Oros, G. *Environ. Int.* **2004**, *30*, 953–971.
6. Kozlowski, C. A.; Walkowiak, W. *Water Res.* **2002**, *36*, 4870–4876.
7. Rio, S.; Delebarre, A. *Fuel* **2003**, *82*, 153–159.
8. Guo, Z.; Chen, R.; Xing, R.; Liu, S.; Yu, H.; Wang, P.; Li, C.; Li, P. *Carbohydr. Res.* **2006**, *341*, 351–354.
9. Guo, Z.; Chen, R.; Xing, R.; Liu, S.; Yu, H.; Wang, P.; Li, C.; Li, P. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4600–4603.
10. Gerente, C.; Lee, V. K. C.; Le Cloirec, P.; McKay, G. *Crit. Rev. Env. Sci. Technol.* **2007**, *37*, 41–127.
11. Dos santos, J. E.; Dockal, E. R.; Cavalheiro, E. T. G. *Carbohydr. Polym.* **2005**, *60*, 277–282.
12. Vasconcelos, H. L.; Camargo, T. P.; Gonçalves, N. S.; Neves, A.; Laranjeira, M. C. M.; Fávere, V. T. *React. Funct. Polym.* **2008**, *68*, 572–579.
13. Karunakaran, S.; Kandaswamy, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1595–1598.
14. Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*; Methuen and Co Ltd: London, 1969.

15. Ngah, W. S. W.; Endud, C. S.; Mayanar, R. *React. Funct. Polym.* **2002**, *50*, 181–190.
16. Inukai, Y.; Chinen, T.; Matsuda, T.; Kaida, Y.; Yasuda, S. *Anal. Chim. Acta* **1998**, *371*, 187–190.
17. Justi, K. C.; Fávere, V. T.; Laranjeira, M. C. M.; Neves, A.; Casellato, A. *Macromol. Symp.* **2005**, *229*, 203–208.
18. Demetgül, C.; Serin, S. *Carbohydr. Polym.* **2008**, *72*, 506–512.
19. Yang, Z.; Shu, J.; Zhang, L.; Wang, Y. *J. Appl. Polym. Sci.* **2006**, *100*, 3018–3023.
20. Guinesi, L. S.; Cavalheiro, E. T. G. *Carbohydr. Polym.* **2006**, *65*, 557–561.
21. Yang, Z.; Zhuang, L.; Tan, G. *J. Appl. Polym. Sci.* **2002**, *85*, 530–535.
22. Sajomsang, W.; Tantayanon, S.; Tangpasuthadol, V.; Daly, W. H. *Carbohydr. Polym.* **2008**, *72*, 740–750.
23. Ding, P.; Huang, K. L.; Li, G. Y.; Zeng, W. W. *J. Hazard. Mater.* **2007**, *146*, 58–64.
24. Krishnapriya, K. R.; Kandaswamy, M. *Anal. Sci.* **2008**, *24*, 1045–1048.
25. Yi, Y.; Wang, Y.; Ye, F. *Colloids Surf., A* **2006**, *277*, 69–74.
26. Sun, S.; Wang, A. *Sep. Purif. Technol.* **2006**, *49*, 197–204.
27. Justi, K. C.; Laranjeira, M. C. M.; Neves, A.; Mangrich, A. S.; Fávere, V. T. *Polymer* **2004**, *45*, 6285–6290.
28. Sun, S.; Wang, A. *J. Hazard. Mater.* **2006**, *131*, 103–111.
29. Hwang Chen, A.; Chang Liu, S.; Chen, C.-Y. *J. Hazard. Mater.* **2008**, *154*, 184–191.
30. Gao, Y.; Lee, K. H.; Oshima, M.; Motomizu, S. *Anal. Sci.* **2000**, *16*, 1303–1308.
31. Varma, A. J.; Deshpande, S. V.; Kennedy, J. F. *Carbohydr. Polym.* **2004**, *55*, 77–93.
32. Justi, K. C.; Fávere, V. T.; Laranjeira, M. C. M.; Neves, A.; Peralta, R. A. *J. Colloid Interface Sci.* **2005**, *291*, 369–374.
33. Vold, I. M. N.; Varum, K. M.; Guibal, E.; Smidsrød, O. *Carbohydr. Polym.* **2003**, *54*, 471–475.
34. Huang, C.; Chung, Y.; Liou, M. *J. Hazard. Mater.* **1996**, *45*, 265–269.