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A new chitosan biopolymer derivative as metal-complexing agent: synthesis, characterization, and metal(II) ion adsorption studies

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ABSTRACT

In this study, a new chitosan biopolymer derivative (CTSL) has been synthesized by anchoring a new vanillin-based complexing agent or ligand, namely 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde, (L) with chitosan (CTS) by means of condensation. The new material was characterized by elemental (CHN), spectral (FTIR and solid state ¹³C NMR), thermal (TG-DTA and DSC), structural (powder XRD), and morphological (SEM) analyses. The CTSL was employed to study the equilibrium adsorption of various metal ions, namely, Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II), as functions of pH of the solutions. Its kinetics of adsorption was evaluated utilizing the pseudo first order and pseudo second order equation models and the equilibrium data were analyzed by Langmuir isotherm model. The CTSL shows good adsorption capacity for metal ions studied in the order Cu(II) > Ni(II) > Cd(II) > Cd(II) > Ni(II) > Cd(II) > Cd(II) > Ni(II) > Cd(II) > Cd(II) > Ni(II) > Cb (II) > Pb(II) in all studied pH ranges due to the presence of many coordinating moieties present in it.

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1. Introduction

Biosorption has recently received a great deal of attention due to the low cost of the materials used in these applications and for the environmentally friendly impact of the treatment of exhausted sorbents. Several types of biomass have been tested for the recovery of precious metals, including fungal biomass,^{1,2} algal biomass but also polymers of biological origin.³ Chitosan (CTS) (hetero polymer constituted of glucosamine and a fraction of acetylglucosamine residues) is a well-known biopolymer characterized by its high sorption properties due to its high nitrogen content. This biopolymer and its derivatives have great potential applications in the areas of biotechnology, biomedicine, food ingredients, and cosmetics because of their many useful features such as hydrophilicity, biocompatibility, biodegradability, anti-bacterial property, and remarkable affinity for many bio-macromolecules.⁴⁻⁸ The presence of amino groups in the polymeric chain of chitosan leads to the possibility of several chemical modifications, including the preparation of Schiff bases by reaction with aldehydes and ketones.^{9,10} The reaction of chitosan with aromatic aldehydes in acetic acid to produce the corresponding Schiff bases has been described by Tirkistani.¹¹ Its attractiveness as an analytical reagent arises from the fact that they enable simple and inexpensive determinations of various organic and inorganic substances.¹² The insertion of functional groups in the chitosan

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matrix may improve its capacity for interaction with metallic ions by complexation, thereby increasing their adsorption properties.^{13,14} In this sense the modification of chitosan with aldehydes to produce Schiff bases may result in a potentially complexing material for metallic species with potential analytical and environmental applications.^{15,16}

With growing interest in the chemical modification of chitosan,^{17–21} a new chitosan derivative, CTSL, was synthesized using substituted vanillin namely 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde (L). The complexing agent or ligand is anchored to chitosan in order to develop a new adsorbent for metal ions. The characterization of the product has been performed by elemental analysis, FTIR, and solid state ¹³C NMR spectroscopy. This material was also employed to study the kinetics and the equilibrium adsorption of various metal ions such as Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II) as functions of the pH solution.

2. Experimental

2.1. Materials

Chitosan of 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 used as received. 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





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were standardized with a standard solution of 0.01 mol L⁻¹ EDTA.²² 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 Atomic Absorption Spectroscopy. Working standard solutions of all 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 used as received.

2.2. Synthesis of the ligand: 4-hydroxy-3-methoxy-5-[(4-methylpiperazin-1-yl)methyl] benzaldehyde (L)

Formaldehyde solution (37%) (2 mL 0.025 mol) was added dropwise with stirring to N-methylpiperazine (2.0 g, 0.02 mol) in ethanol (20 mL) at 60 °C. Then, the stirring was further continued for an hour and a solution of 4-hvdroxy-3-methoxy benzaldehvde (3.04 g, 0.02 mol) dissolved in 60 mL of ethanol was added to it and refluxed for 18 h. After refluxing, the solvent was removed by distillation under vacuum using rotary evaporator and the residue was extracted with chloroform. The white colored solid was recovered after removing the chloroform by distillation. It was then further purified by silica gel column chromatography using chloroform-light petroleum ether (bp 60-80 °C, 1:9 v/v) as the eluent. The product was obtained by slow evaporation of the eluted solvent as white colored crystals. Yield: 4.0 g (76%). mp: 118 °C. Analytical data for C₁₄H₂₀N₂O₃; Calcd: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.60; H, 7.52; N, 10.56. Mass (EI) *m/z*: 264 (M⁺). Selected FT-IR data (KBr, $v \text{ cm}^{-1}$): 3445, 1641, 1592, 1472. ¹H NMR (CDCl₃, δ ppm): 2.31 (s, NCH₃, 3H), 2.60 (br s, N-CH₂-CH₂-N, 8H), 3.82 (s, N-CH₂-Ar, 2H), 3.94 (s, CH₃O, 3H), 7.17 (s, Ar-H, 1H), 7.34 (s, Ar-H, 1H), 9.77 (s, CHO, 1H). ¹³C NMR (CDCl₃, δ ppm): 45.7 (N-CH₃), 52.3, 54.6 (N-CH₂-CH₂-N), 55.9 (N-CH₂-Ar), 60.6 (-OCH₃), 109.5, 120.6, 125.5, 128.2, 148.6, 153.9 (ArC), 190.6 (CHO). Single Crystal Analysis CCDC No.: 673897.

2.3. Synthesis of the chitosan biopolymer derivative (CTSL)

Chitosan powder 1.0 g (0.0048 mol of glucosamine residue) was dissolved in 25 mL of 1 wt % acetic acid and diluted with methanol (150 mL). Then 1.6 g of 4-hydroxy-3-methoxy-5-[(4-methylpipera-zin-1-yl)methyl] benzaldehyde (L) (0.006 mol) dissolved in chloroform (20 mL) was added slowly to it. The mixture was stirred at room temperature for 16 h, followed by refluxing for 18 h, which resulted in a brown colored gel. It was then decanted and thoroughly washed with chloroform to remove any unreacted L and then dried in vacuum at 60 °C to give CTSL as a brown colored powder. Yield: 1.87 g (72%). *Analytical data for CTSL* ($C_{20}H_{29}N_2O_6$): Found: C, 46.52; H, 6.01; N, 6.55. ¹³C NMR (Solid State, δ ppm): 23.1, 59.0, 73.9, 81.9, 102.8, 126.1, 159.0. Selected FT-IR data (KBr, ν cm⁻¹): 3431, 1638, 1404, 1033, 750, 649.

2.4. Preparation of metal-CTSL

The metal complexes of the chitosan derivative were prepared by the addition of 50.0 mL of 100 mg L⁻¹ of metal ion (Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II)) solutions buffered at pH 7.5 to 50 mg sample of chitosan derivative (CTSL) for a period of 4 h by agitation. After 4 h the shaking was turned off and immediately thereafter the adsorbent material was decanted and dried at 60 °C.

2.5. Instrumentation

Elemental analyses were carried out on a Carlo Erba model 1106 elemental analyzer. Fourier transform infrared spectra (FTIR) were recorded on a Perkin–Elmer RX1 model spectrophotometer on KBr disks in the wavenumber range 4000–250 cm⁻¹. ¹H NMR and ¹³C NMR spectra were recorded using a model FX-80-Q Fourier transform nuclear magnetic resonance spectrometer. TG and DTG analyses were carried out with 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 K α 1 radiation with a quartz monochromator. Micrographs of CTSL 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).

2.6. Adsorption experiments

2.6.1. Effect of pH on adsorption

The adsorption properties of chitosan derivative and the effect of the pH on adsorption were studied from pH 3 to 10 utilizing various buffer solutions (KCl/HCl for pH 2 and 3; acetic acid/sodium acetate for pH 4, 5, and 6; tris(hydroxymethyl) aminomethane/ HCl for pH 7.5 and 8.5; and ammonia/ammonium chloride for pH 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 chitosan derivative for a period of 2 h by agitation. 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 (II) ions adsorbed at different pH values was calculated with the following Eq. 1:^{23,24}

$$Q_e = \frac{(C_0 - C_e)V}{W},\tag{1}$$

where Q_e is the equilibrium adsorption capacity of the vanillinbased chitosan derivative CTSL (mg g⁻¹ adsorbent), *V* is the volume of solution (mL), C_0 and C_e are the initial and equilibrium concentration of the solute in (mg L⁻¹), respectively, and *W* is the weight of the sorbent (g).

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

$$q_e = \frac{(C_0 - C_e)V}{WM},\tag{2}$$

where q_e is the adsorption capacity of the adsorbent at equilibrium in mmol metal ion/g adsorbent and M is the atomic weight of the corresponding metal ion.

2.6.2. Adsorption kinetics

The adsorption kinetics of the new chitosan material was determined at pH 8.5. A 50 mg of chitosan derivative and 50.0 mL of Cu(II) ion solutions buffered at 8.5 were shaken using an orbital shaker at 200 rpm for 2 h. After pre-determined time periods, 2 mL aliquots were removed and the concentrations of Cu(II) ions in solutions were measured.

2.6.3. Adsorption equilibrium isotherms

Samples of the chitosan derivative (50.0 mg) were added to 25.0 mL of Cu(II) ion solution in several concentrations and previously buffered to the optimum adsorption pH. After this procedure, they were kept under stirring until the adsorption equilibrium was reached. Aliquots were taken and diluted in order to determine metal ion concentration by AAS. It was observed that the adsorption process was fast and reached equilibrium after 2 h and remained constant for 24 h.

3. Results and discussion

3.1. Synthesis and characterization of vanillin-based ligand

The vanillin-based ligand or complexing agent L was prepared by the Mannich base reaction of 4-hydroxy-3-methoxy benzaldehyde (vanillin) with equivalent amounts of formaldehyde and secondary amine namely *N*-methyl piperazine as shown in Scheme 1. The compound was characterized by FTIR and ¹H and ¹³C NMR spectral techniques. The FT-IR spectra of the compound exhibit a band around 3410–3420 cm⁻¹ due to the stretching of v(-OH)group. The band around 1640 cm⁻¹ is observed due to the presence of v(C=O) of aldehyde group of the compound. The band around 1590 cm⁻¹ is appeared due to the presence of v(C=C) stretching of aromatic group. The band around 1470 cm⁻¹ indicates the $v(-O-CH_3)$ bending of methoxy methyl group of the compound. The ¹H NMR spectrum of the compound exhibits a singlet peak around 9.77 ppm due to the presence of aldehydic proton. The peak at 7.17 ppm appeared due to the two aromatic protons. The



Scheme 1. Synthesis of new vanillin-based ligand (L).

singlets in the region around 3.80–3.95 ppm are observed due to methoxy and benzylic protons. Broad singlet is obtained around 2.60 ppm for piperazine N–CH₂ and N–CH₃ protons of L. The ¹³C NMR spectrum of the compound showed peaks in the region around 45, 52–54, 65, 109–154, and 190 ppm indicating the presence of N–CH₂, Ar-CH₂, O–CH₃, aromatic(C), and CHO carbons, respectively.²⁵

3.2. X-ray diffraction studies

The molecular formula of L is $C_{14}H_{20}N_2O_3$. The compound crystallizes in the monoclinic space group P21/n with one molecule in the unit cell. The dimension of the unit cell is a = 14.4364(7) Å, b = 6.0102(3) Å, c = 16.5733(8) Å, $\beta = 107.13(1)^\circ$, Z = 4. The molecular structure was solved by direct methods and refined by full-matrix least-squares procedures. SHELXS97 and SHELXL97 programs are used for structure solution and structure refinement,²⁶ respectively. The crystal structure of L is as shown in Figure 1 and the crystal data are given in Table 1. CCDC No.: 673897.

3.3. Synthesis and characterization of CTSL

The new chitosan derivative CTSL was obtained by condensation of chitosan with equivalent amounts (glucosamine units) of vanillin-based ligand L. The reaction between aldehyde group from ligand and amine groups from chitosan provides Schiff base formation in the polymeric structure as shown in Scheme 2. The ligand introduces coordinating groups into the chitosan, such as phenolic group, imine group, and piperazine unit, conferring metal ion chelation properties to the new adsorbent. Hence, the new adsorbent has a special characteristic, in that it contains ligand capable of coordinating to metal ions in solution anchored to them.

3.3.1. Elemental analysis

The *C*/*N* ratio from the elemental analysis data of chitosan and its new derivative CTSL are found to be 6.05 and 7.10, respectively.



Figure 1. Single crystal ORTEP diagram of L.

Table 1		
Crystal data	and structure	refinement

Empirical formula	$C_{14}H_{20}N_2O_3$
CCDC No.	673897
Formula weight	264.32
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	
a (Å)	14.4364(7)
b (Å)	6.0102(3)
<i>c</i> (Å)	16.5733(8)
α (°)	90.00
β(°)	107.13(1)
γ (°)	90.00
Volume (Å ³)	1397.21(12)
Ζ	4
Density (calcd) (Mg/m ³)	1.257
Absorption coefficient (mm ⁻¹)	0.089
F(0 0 0)	568
Crystal size (mm)	$0.24 \times 0.20 \times 0.20$
Index ranges	$-21 \leqslant h \leqslant 21, -8 \leqslant k \leqslant 8, -24 \leqslant l \leqslant 24$
Reflections collected	19354
Independent reflections	4806 [<i>R</i> (int) = 0.0247]
Completeness to 2θ	99.8%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4806/0/185
Goodness-of-fit on F ²	1.042
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0501$, $wR_2 = 0.1456$
R indices (all data)	$R_1 = 0.0741, wR_2 = 0.1638$
Largest diff. peak and holes ($e Å^{-3}$)	0.265 and -0.193

for L

The degree of substitution (*DS*) of the ligand, L to $-NH_2$ group on chitosan is calculated by the following equation:²⁷

$$DS = \frac{a(C/N)_m - (C/N)_o}{n}$$
(3)

where $(C/N)_m$ is the C/N ratio of the modified chitosan derivative, $(C/N)_o$ is the C/N ratio of the original chitosan, and 'a' and 'n' are the number of nitrogen and carbon introduced after chitosan modification, respectively. The DS obtained for CTSL is 0.54.

3.3.2. FT-IR and solid state ¹³C NMR analysis

The FT-IR spectra of the CTS and CTSL are shown in Figure 2a and b, respectively. The FT-IR spectrum of CTS exhibits a strong peak at 3446 cm⁻¹ which can be assigned to axial stretching vibra-

tion of O-H superimposed to the N-H stretching band and the inter hydrogen bonds of the polysaccharide. The band due to C-H stretching appears at 2929 cm^{-1} . The band at 1637 cm^{-1} indicates the presence of CTS-NHAc (acetyl) units (with >C=O stretching). The bands at 1144 cm⁻¹ (asymmetric stretching of the C–O–C bridge), 1067, and 1031 cm^{-1} (skeletal vibrations involving C–O stretching) are characteristic of chitosan's saccharide structure.²⁹⁻³² The FT-IR spectrum of the chitosan derivative shows an additional peak around 3420 cm⁻¹ for phenolic –OH group apart from a strong peak at 3440-3470 cm⁻¹ for CTS, corresponding to the stretching vibration of -N-H group and -OH group. The splitting of the band in the region around 1638 cm⁻¹ indicates the presence of imine (>C=N) group in the derivative. The band at 1067 cm^{-1} assigned to the stretching vibration of secondary >C-OH group shifts toward lower wavelength 1033 cm⁻¹, which may be due to steric effect resulting from the condensation of ligand to CTS. Further, peaks around 1400 cm⁻¹ are due to aromatic backbone vibration and a peak around 1250 cm^{-1} is due to phenolic C–O group of the ligand moiety.^{28,30} The high-resolution solid state ¹³C NMR is used for characterization of new adsorbent and the ¹³C NMR spectra of CTS and CTSL are shown in Figure 3a and b, respectively. When compared to CTS, the ¹³C NMR spectrum of CTSL shows additional peaks in the region 120-180 ppm which are attributed to the aromatic carbon atoms present in the chitosan derivative. The difference in the nature and intensity of peaks in the region 20-110 ppm of CTSL when compared to CTS^{25,26} indicates that the additional aliphatic carbon atoms are present in the derivative.

3.3.3. Thermal analysis

The TG-DTA curves of CTS and CTSL are shown in Figure 4a and b, respectively. The chitosan shows thermal degradation at two stages, one at 73 °C with a 22% loss and another at 324 °C with a 41% loss in polymer mass. The thermal degradation of CTSL occurs at two different ranges of temperatures namely 65 °C and 306 °C with different percentage weight loss of 19% and 37%, respectively. The first one is due to water elimination which adsorbed physically to the biopolymer matrix and the second one may be due to the dehydration of the saccharide rings, depolymerization, and decomposition of the polymer. The main thermal degradation process of CTSL takes place at temperature lower than the secondary degradation stage of chitosan indicating that the CTSL polymer is less stable than the chitosan. It seems that the instability of the CTSL polymer compared to the chitosan may be due to the decrease in



Scheme 2. Synthesis of new chitosan biopolymer derivative (CTSL).



Figure 2. The FTIR spectra of (a) CTS and (b) CTSL.

the number of primary amino groups after chemical modification process,²⁹ whereas, the DSC thermogram for chitosan²⁴ showed a wide endothermic peak at 111 °C and an exothermic peak at 305 °C. The DSC thermograms for the chitosan and its derivative are given in Figure 5a and b, respectively. The chitosan derivative exhibits endothermic peaks in the region 72 °C and exothermic peaks in the region 325 °C. It is well known that for chitosan and its derivatives the endothermic peaks observed for water vapor elimination in the polymer matrix and the exothermic peaks observed for the decomposition of the polymer²⁹ and these differences in thermograms of chitosan and its derivative may be caused by the chemical modification.³²

3.3.4. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of CTS and CTSL are given in Figure 6a and b, respectively. The CTS shows the characteristic sharp 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 (002). The studies indicate that the intensity of peaks at $2\theta = 10$ °C and 20 °C of CTSL decreases also with the broadening of peaks when compared to free chitosan. This indicates that the crystallinity of modified chitosan derivative decreases. This decrease in crystallinity of chitosan derivative is attributed to the deformation of the strong hydrogen bond in the free chitosan molecule and also due to the substitution of ligand on it. This indicates that CTSL is less crystalline and more amorphous than free chitosan.^{32,34}

3.3.5. SEM analysis

The difference in structural morphology between chitosan and CTSL is further supported by the difference in their SEM images. The SEM images of the surface of CTS and its derivative are shown in Figure 7a and b, respectively. The chitosan derivative displayed a more extensive three-dimensional network compared to the smooth lacunose surface of chitosan and it is attributed to the condensation of vanillin-based complexing agent on polymer surface.^{29,33}



Figure 3. The solid state ¹³C NMR spectra of (a) CTS and (b) CTSL.

3.4. Preparation and characterization of metal-CTSL

The metal complexes of the chitosan derivative were prepared by the adsorption of one mole of metal(II) ions such as Mn(II), Fe(II), Co(II), Cu(II), Ni(II), Cd(II), and Pb(II) ions on equimolar chitosan derivative (glucosamine unit) in aqueous solution (pH 7.5). The proposed schematic representation of structure for the metal-complexed chitosan derivative [M-(CTSL)] is shown in Scheme 3. The resulting [M-(CTSL)] is characterized using FTIR spectral analysis and SEM analysis. The FTIR spectra of [Cu-(CTSL)] when examined showed adsorption bands at 514 and 462 cm⁻¹ due to stretching vibration of N–Cu and O–Cu, respectively. Further, new bands near 600–500 cm⁻¹ indicated the presence of SO₄^{2–} ions in the resulting copper complex of chitosan derivative.

The SEM images for [Cu-(CTSL)] and [Co-(CTSL)] are shown in Figure 7c and d, respectively. It is observed that the surface of the metal-complexed derivatives exhibits more pores when compared to CTS or its derivative which may be due to the metal sites coordinated to chitosan derivative.^{33–35}

3.5. Adsorption studies

3.5.1. Effect of pH on adsorption

The effect of pH on adsorption of metal ions by vanillin-based chitosan derivative CTSL is illustrated in Figure 8. From this study,

we infer that the adsorption capacity of modified chitosan derivative is affected by the pH. The metal(II) ion adsorption by CTSL increases with the pH of the solution from 3.5 to a maximum value of 6.5 and then decreases with further increase in pH. At acidic pH 3.5-5.5, the lower adsorption of metal ions is attributed to the protonation of the complexation site (amine), which decreases the complex formation by the chitosan derivative with metal ion.^{36,37} Around pH 6.5-7.0 the amino group exists as free amine (without protonation) and in addition, the deprotonation takes places at phenolic group present in the chitosan derivative which increases the metal ion uptake by the adsorbent. The buffer solution, tris(hydroxymethyl) aminomethane/HCl used for pH 7.5 and 8.5, can form complexes with the metal ion in order to avoid precipitation of metal hydroxide. This complex formation decreases the metal ion uptake by the CTSL. From the studies, we found that the binding capacities of the derivative for Mn. Fe. Co. Cu. Ni. Cd. and Pb were 19.8, 18.4, 22.4, 56.5, 34.6, 46.1, and 51.8 mg/g, respectively, and these values are higher than the values obtained for unmodified chitosan.^{10,17,18,21} The results also indicate that the new adsorbent has a good adsorption capacity for Cu(II) ions, in the pH ranges studied, suggesting possible selectivity for this metal ion and thus following the order of binding capacity in mmol g^{-1} for the derivative as $Cu(II) > Ni(II) > Cd(II) \ge Co \ge Mn(II) > Fe(II) > P$ b(II). This sequence maintained the trend in the well-known Irvin-Williams series.^{37,38} The CTSL forms more stable complex with copper(II) ions in aqueous solution than other metal ions studied and hence shows maximum adsorption toward Cu(II) ions (see Fig. 9).

3.5.2. Adsorption kinetics

Kinetics of adsorption is one of the most important characteristics to be responsible for the efficiency of adsorption. Traditionally, the kinetics of interaction at solid/solution interface is described following the expressions originally given by Lagergren which are special cases for the general Langmuir rate equation.³⁹ The fitting validity of these models is traditionally checked by the pseudo first order and pseudo second order models to interpret the experimental data. A good correlation of the kinetics data explains the adsorption mechanism of the metal ion on the solid phase.

The pseudo first order equation was represented by Eq. 4:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t$$
 (4)

where k_1 (min⁻¹) is the pseudo first order adsorption rate constant, Q_t is the amount adsorbed at time t (min), and Q_e denotes the amount adsorbed at equilibrium, both in mg g⁻¹. The plots of log $(Q_e - Q_t)$ versus t gave the k_1 and Q_e values.

The pseudo second order equation, based on adsorption capacity at equilibrium, can be expressed by Eq. 5:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$$
(5)

where k_2 (g mg⁻¹ min⁻¹) is the adsorption rate constant of pseudo second order and Q_e can be obtained from the intercept and slope of the plot of (t/Q_t) versus t.

The adsorption kinetics studies for CTSL toward Cu(II) show the first order and second order rate constants k_1 and k_2 to be 1.8×10^{-2} min⁻¹ (Q_e , cal = 29.1 mg g⁻¹ with R = 0.934) and 1.4×10^{-3} g mg⁻¹ min⁻¹ (Q_e , cal = 58.1 mg g⁻¹ with R = 0.999), respectively. Based on the obtained correlation coefficients R, and the experimental and calculated Q_e values, the pseudo second order equation was the model that showed the best fit for the experimental kinetics data and not the pseudo first order kinetics equation. This indicates that



Figure 4. The TG-DTA curves of (a) CTS and (b) CTSL.

chemical sorption is the rate-limiting step of adsorption mechanism and not involving a mass transfer in solution.³⁹

3.5.3. Adsorption isotherms

An adsorption isotherm, the relation between the amounts of solute adsorbed (Q_e) and the remaining concentrations in the aqueous phase (C_e), is basically important to describe how adsorbate interacts with adsorbent and so is critical in optimizing the use of sorbents. Therefore, correlation of equilibrium data by a theoretical equation is necessary to practical operation. In the past, the Langmuir equation^{39,40} has been used to correlate isotherm data for the sorption of metal ions and organic solutes on to raw and substituted chitosan derivative.

The equilibrium studies were carried out for this derivative 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, it is found that the adsorption capacity increased with the equilibrium concentration of the metal ion in solution, progressively reaching saturation of adsorbent. The following Langmuir equation 6 takes into account adsorption sites with the same energy, where the formation of a monolayer occurs on the surface of the adsorbent with saturation of the sites:

$$Q_e = \frac{K_L C_e Q_m}{1 + K_L C_e} \tag{6}$$

where Q_e and C_e are the amount adsorbed (mg g⁻¹) and the adsorbate concentration in solution (mg L⁻¹), respectively, both at equilibrium. K_L (L g⁻¹) is the Langmuir constant and Q_m (g mg⁻¹) is the maximum adsorption capacity for monolayer formation on adsorbent. The linear form of the Langmuir isotherm, represented by Eq. 7, is employed to determine the K_L and Q_m values from linear and angular coefficients obtained by:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{7}$$



Figure 5. The DSC thermogram of (a) CTS and (b) CTSL.



Figure 6. The powder X-ray diffraction patterns of (a) CTS and (b) CTSL.



Figure 7. SEM image of (a) CTS, (b) CTSL, (c) Cu-CTSL, and (d) Co-CTSL.



Scheme 3. Structure of metal complex of the new chitosan derivative.

The Q_m values were calculated for CTSL according to Langmuir isotherm model. The results obtained from adsorption isotherms for various metal(II) ions according to the Langmuir model are given in Table 2 and it shows good correlation coefficients (R > 0.99) with the experimental data from adsorption equilibrium of metal ions, suggesting homogeneous adsorption, which means a monolayer.³⁹

The nature and the number of coordination sites present in the chitosan polymer influences the adsorption capacity of chitosan derivative. From the present study, we infer that the anchoring of chitosan with vanillin-based complexing agent enhances the adsorption capacities of adsorbent when compared to free chitosan and chitosan derivative with mere vanillin which may be due to polydentate moiety containing nitrogen and hydroxo donors being present in it.

3.6. EPR studies

In order to interpret the complexation of modified chitosan derivative with Cu(II) ions, EPR studies at room temperature on the copper-adsorbed chitosan derivative were carried out. The studies showed an axial EPR spectrum (Fig. 6) for copper-adsorbed chitosan derivative [M-(CTSL)] typical to mononuclear metal–ligand [Cu(II)-(L)] complex at liquid nitrogen temperature⁴¹ and the parameters were found to be g_{\parallel} (g_{\perp}) as 2.26 (2.03) and A_{\parallel} as 157.9 for [Cu-(CTSL)]. This is suggestive of a tetragonally distorted octahedral, square pyramidal, or square-planar geometry having a



Figure 8. Effect of pH on metal(II) ion adsorption by CTSL. $\{[M^{2+}] = 100 \text{ mg } L^{-1};$ temperature = 25 °C; contact time = 2 h; shaking rate = 200 rpm; adsorbent mass = 50 mg}.



Figure 9. EPR spectrum of Cu-CTSL.

Table 2

Parameters for various metal(II) ion adsorption by CTSL according to Langmuir isotherm model {where, K_L (L g⁻¹) is the Langmuir constant and Q_m is the maximum adsorption capacity for monolayer formation on adsorbent expressed in mg g⁻¹ and m mol⁻¹}

Metal(II) ion	Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(II)	Cd(II)	Pb(II)
$K_{\rm L} ({\rm Lmg^{-1}}) \times 10^{-2}$	4.9	4.9 43.1	3.0 31.2	2.5	1.9	4.9	7.5
$Q_{\rm m}$, cal (m mol ⁻¹)	0.89	0.59	0.38	0.36	0.33	0.41	0.25

 $dx^2 - y^2$ ground. Therefore, the EPR data clearly demonstrate that there is a mononuclear type of interaction between chitosan derivative and Cu(II) ions in [M-(CTSL)].²⁴

4. Conclusion

A new chitosan derivative was synthesized by the chemical modification of chitosan with vanillin-based complexing agent. It was then characterized by various techniques such as elemental, spectral, and structural analysis. The binding capacities of the derivative for Mn, Fe, Co, Cu, Ni, Cd, and Pb are found to be 19.8, 18.4, 22.4, 56.5, 34.63, 46.1, and 51.8 mg/g, respectively, and were very higher than the values obtained for unmodified chitosan. The morphological studies conducted using SEM indicate the adsorption of metal ions on the biopolymer surface. The higher adsorption capacity toward Cu(II) ions than the other metal ions studied indicates that it shows selectivity toward Cu(II) ions in aqueous solution and hence it can be used to extract Cu(II) ion from the industrial waste water.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.06.005.

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