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Synthesis of ethylenediamine modified chitosan and evaluation for removal of divalent metal ions

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ABSTRACT

Selective modification of chitosan has been achieved by incorporating ethylene-1,2-diamine molecule in a regioselective manner using N-phthaloylchitosan and chloro-6-deoxy N-phthaloylchitosan as precursors. The present modification results in additional nitrogen centres which function as potential binding sites during adsorption of metal ions. The derivative ethylene-1,2-diamine-6-deoxy-chitosan and its pthaloylated precursor have been evaluated for divalent metal ion removal. The former is found to have higher capacity for adsorption due to the presence of additional —NH_2 group. The samples exhibited highest affinity for Cu and least for Zn. About 80% of the adsorbed metal ions could be stripped in a solution of pH 1.2. The interaction between acidic metal centres and basic nitrogen centres on surface of the adsorbent appears to govern adsorption. Intrachain and interchain co-ordinate bonding involving NH and NH_2 groups is proposed to be the mechanism of formation of metal–adsorbent complex. The adsorption process is described by Langmuir model.

1. Introduction

Environmental pollution has always been a serious issue, especially regarding heavy metal ions. Heavy metals are considered to be the most dangerous polluting agents in water. The danger is due to their bioaccumulation and non-biodegradability (Nica, Bura, Gergen, Harmanescu, & Bordean, 2012).

Adsorption is one of the most economical, effective and widely used methods for the removal of toxic metals from aqueous environments. The great advantage of this method over others is the low generation of residues, easy metal recovery and the possibility of reuse of the adsorbent. Studies have been carried out to develop more effective and selective adsorbent materials, which are abundant in nature and require minimal processing in order to the decrease cost (Ng, Cheung, & McKay, 2003; Vasconcelos, Guibal, Laus, Vitali, & Favere, 2009).

The application of biopolymers as adsorbents is an emerging technique and is of interest in studies on the removal of metal ions from aqueous solutions. Special attention has been given to the biopolymer, chitosan (Findon, McKay, & Blair, 1993). Chitosan has a large capacity for the fixation of molecules such as pesticides, proteins, and dyes. The free amino function of chitosan gives it a better ability to chelate ions of transition metals than other natural polymers such as cellulose and its derivatives. The chelating properties are utilized for water treatment and particularly to recover metals (Muzzarelli, 2011). It has been found that cross linking reduces the adsorption capacity of the chitosan. The main reason for the loss of adsorption capacity is the involvement of amine groups in the cross-linking reaction (Ngah, Endud, & Mayanar, 2002). The ability of chitosan to capture metal ions can be enhanced by suitable modification of the molecule. The amino and two hydroxyl groups on each glucosamine in the repeating unit of chitosan can act as reactive sites for chemical modification. Several such studies have been reported in the literature on the enhancement of adsorption ability of chitosan and and adsorption selectivity (Ramesh, Hasegawa, Sugimoto, Maki, & Ueda, 2008; Zhou, Wang, Liu, & Huang, 2009; Guo et al., 2005).

In the present investigation, modification of Cts has been attempted by substitution of ethylenediamine molecule at C-6 position in highly regioselective manner. This modification has been carried out with an idea of enhancing the metal binding capacity of the compound due to the presence of additional 'N' centres incorporated during modification.

2. Experimental

2.1. Materials

Chitosan (Cts) was purchased from Sigma–Aldrich (India). Phthalic anhydride, N,N′-dimethylformamide (DMF), thionylchloride($SOCl_2$), ethylene-1,2-diamine(En), hydrazine hydrate, N-methyl-2-pyrrolidone (NMP), copper sulphate, lead

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nitrate, nickel sulphate, zinc sulphate, potassium chloride and hydrochloric acid were all reagent grade and purchased from Spectrochem (India). The reagents were used without prior purification.

2.2. Synthesis

2.2.1. Synthesis of N-phthaloylchitosan (PtCts)

Phthaloyl chitosan was synthesized according to a previous method (Torii, Ikeda, Shimojoh, & Kurita, 2009). A sample of 1.0 g chitosan was reacted with 4.04 g of phthalic anhydride in 20-mL of DMF/water (95/5) at 120 °C with stirring under nitrogen. The mixture turned into a viscous dispersion in about 1.5 h and then to a gelatinous mass in 2 h. The reaction was continued and after 8 h, the mixture was cooled to room temperature and the product was precipitated in 500 mL of ice water. The solid product, represented as *PtCts*, was washed with methanol and dried to give 1.62 g (90%) of white powdery material.

2.2.2. Synthesis of chloro-6-deoxy-N-phthaloylchitosan (PtCtsCl)

A sample of 2.0 g of PtCts was dispersed in 25-mL of DMF and stirred for 2 h at 80 °C on a water bath. 0.9-mL $SOCl_2$ was added and the mixture was further maintained under stirring at 80 °C. After 2 h, the mixture was cooled to room temperature, the yellow powdery product, designated as *PtCtsCl*, was filtered, washed with acetone and dried.

2.2.3. Synthesis of ethylene-1,2-diamine-6-deoxy-**N**-phthaloylchitosan (PtCtsEn)

A sample of 1 g of PtCtsCl was dispersed in 50-mL of DMF and stirred for 2 h at 80 °C on a water bath. 5 mL of En was added and the mixture was further heated at 80 °C. After 2 h, the mixture was cooled to room temperature, the product, designated as *PtCtsEn*, was filtered, washed with water and dried.

2.2.4. Synthesis of ethylene-1,2-diamine-6-deoxy-chitosan (CtsEn)

A sample of 0.21 g of PtCtsEn was dispersed in 15 mL of NMP. To the mixture 15 mL of aqueous hydrazine monohydrate (4 M) was added, and the mixture was stirred at 100 °C for 4 h under nitrogen. The product, designated as CtsEn, was filtered, washed with alcohol and dried.

2.3. Characterization

The infrared spectra of the samples, PtCtsCl, PtCtsEn and CtsEn were recorded in KBr pellets on a Shimadzu FTIR spectrometer, model IR-Prestige-21.

TGA was performed with a Shimadzu DTG-60 thermogravimetric analyser. The samples were heated from 0 to 600 °C at the heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Scanning electron micrographs of the samples before and after adsorption of metal ions were recorded on a JEOL-JSM 5800LV scanning electron microscope under a voltage of 20 kV.

The concentration of metal ions in aqueous solutions were determined in mg L^{-1} using Atomic Absorption Spectrometer, GBC 932 plus, calibrated with standard metal ion solutions.

2.4. Adsorption, desorption and competitive adsorption studies

2.4.1. Adsorption studies

The capacity of the ethylenediamine modified chitosan materials to extract metal ions from aqueous solution was determined in duplicate, using a batch process with three divalent metal ions, namely, copper(Cu), lead(Pb), and zinc(Zn). About 10 mg of PtCtsEn or CtsEn was suspended in 25.0 cm^3 of an aqueous solution with concentrations of each metal varying from 5 to 20 mg L^{-1}. After 2 h the suspensions were centrifuged. Aliquot of the supernatant was appropriately diluted and concentration of the metal ion was determined by AAS. The absorption capacity of the material is determined using Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}); C_0 and C_e are the initial and equilibrium liquid phase solute concentration (mg L^{-1}), respectively; v is the liquid phase volume (L) and W is the amount of the absorbent (g). The capacity of the parent compound Cts to extract the above three metal ions was also determined in duplicate, using the metal ion solution of 20 mg L^{-1}, for comparison.

2.5. Desorption

To evaluate the reusability of sorbent materials, PtCtsEn or CtsEn, adsorption experiments were followed by desorption. The adsorption experiments were carried out by suspending about 10 mg of PtCtsEn or CtsEn in 25-mL of metal salt solutions of initial concentration 20 mg L^{-1}. After 2 h, the metal ion adsorbed sample was separated by centrifugation, washed with water and dried. For desorption studies, 10 mg of adsorbed sample was suspended in 25-mL of stripping solution of pH 1.2 (0.2 M KCl and 0.2 M HCl) and stirred for 2 h at room temperature. The suspension was centrifuged. Aliquot of the supernatant was appropriately diluted and the concentration of the desorbed metal ions was determined by AAS.

The percentage of desorption was calculated using Eq. (2).

$$\text{Desorption}\,(\%) = \frac{\text{amount of metal ion desorbed}}{\text{amount of metal ion adsorbed}} \times 100 \quad (2)$$

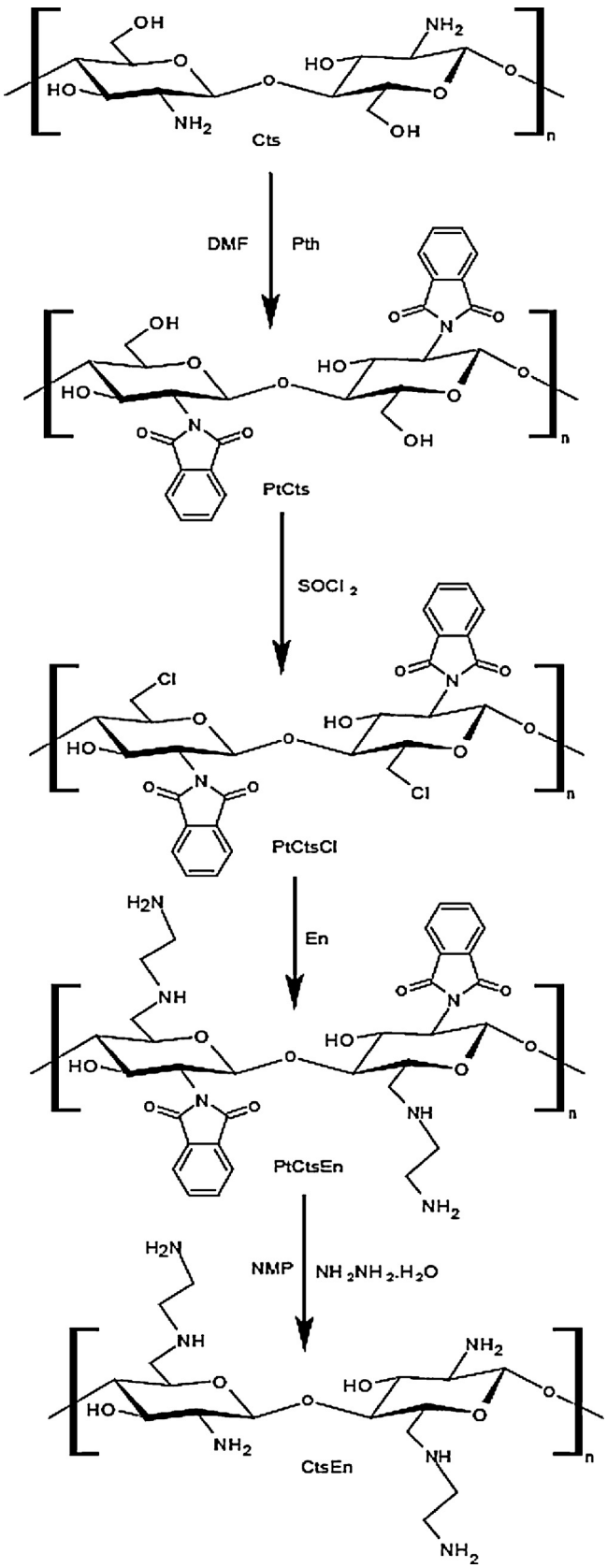
2.6. Competitive adsorption

Competitive adsorption studies were done by suspending 10 mg of PtCtsEn or CtsEn samples in 25 mL of the mixture containing 20 mg L^{-1} of each metal ion, Cu, Pb and Zn. After stirring at room temperature for 2 h the suspension was centrifuged and aliquot of the supernatant was appropriately diluted and concentration of the three metal ions in the supernatant solution was determined by AAS. The amount of metal ions competitively adsorbed was calculated using the Eq. (1).

3. Results and discussion

3.1. Synthesis of PtCtsEn and CtsEn

The synthesis of CtsEn has been accomplished by sequential modification of Cts by 4 reaction steps following the traditional synthetic methodology adopted for derivatisation of polysaccharides such as cellulose and chitosan (Da Silva Filho, De Melo, Da Fonseca, & Airoldi, 2009; Takagai, Shibata, Kiyokawa, & Takase, 2011). As shown in Scheme 1, the selective modification by ethylenediamine group at the C-6 position has been achieved in a highly regioselective manner using N-phthaloylchitosan and chloro-6-deoxy N-phthaloylchitosan as precursors. Phthaloylation of chitosan is proved a convenient technique for protecting the amino functionality and also for solubilisation of Cts in organic solvents (Kurita, Ishizeki, Fujisaki, & Iwakura, 1982; Nishimura, Kohgo, Kurita, & Kuzuhara, 1991). On protection of the amino group at C-2 position of chitosan, regioselective substitution of the hydroxyl group at C-6 position with 'Cl' has been achieved by reaction with $SOCl_2$. As 'Cl' is known to be a good leaving group for the nucleophilic substitution reaction, the chloro-6-deoxy-N-pthaloyl



Scheme 1. Synthesis of PtCtsEn and CtsEn.

chitosan is a potentially useful precursor for the regioselective synthesis of ethylene-1,2-diamine-6-deoxy-chitosan (*CtsEn*). This has been achieved in two steps; by the reaction of chloro-6-deoxy-N-phthaloylchitosan (PtCtsCl) with ethylenediamine followed by dephthaloylation using hydrazine hydrate, leading to regeneration of free amino groups at C-2 position.

3.2. Infrared characterization of chitosan derivatives

The FT-IR spectra of Cts (not shown) exhibit a broad band at around 3443 cm^{-1} attributed to —NH and —OH stretching vibration, as well as inter- and intra-molecular hydrogen bonding. A weak band at 2926 cm^{-1} is attributed to —CH stretching. The two bands at 1640 and1591 cm^{-1} represent bending vibrations of the free amine and acetylated amine, respectively, indicating that the sample is not fully deacetylated. The symmetric stretching of bridge C—O—C is observed at 1160 cm^{-1} and the skeletal C—O stretching appears at 1090 cm^{-1}.

The FTIR spectra of the three derivatives, namely, PtCtsCl, PtCtsEn and CtsEn are shown in Fig. 1.

In the spectrum of PtCtsCl, shown in Fig. 1a, the broadness of the band centred around 3500 cm^{-1} decreases and the band at 1591 cm^{-1} disappears, supporting the substitution of free $-NH_2$ and —OH groups at C-2 and C-6 positions, respectively. Introduction of phthaloyl group is evidenced by the appearance of two sharp bands at 1764 and 1712 cm^{-1} attributed to imide carbonyl group and a band at 721 cm^{-1} due to aromatic C—H deformation. A sharp band at 873 cm^{-1} and a relatively weak band at 796 cm^{-1} support the formation of C—Cl bond.

In the spectrum of PtCtsEn shown in Fig. 1b, the intensity of the peaks at 873 and 796 cm^{-1} decreases, indicating the reaction of Cl with En but are do not disappear completely due to incomplete substitution. N—H peak at 1645 cm^{-1} intensifies and the broadness of the band around 3500 cm^{-1} increases. The band at 2852 cm^{-1} arises due to C—C stretching of En moiety. All these data confirm the formation of PtCtsEn.

In the FT-IR spectra of CtsEn shown in Fig. 1c, peaks at 1716 and 1782 cm^{-1} have disappeared supporting the dephthaloylation reaction.

3.3. Thermogravimetry

The TGA of Cts shown in Fig. 2a indicates the degradation of Cts as a three step process. A weight loss of 10% around 87 °C followed by sharp change of 60% weight loss around 286 °C and the final loss of 30% gradually in the temperature range, 300–600 °C. The three stages correspond to the loss of free and bound water, pyrogenic decomposition and ablation of molecule chains, respectively. Similar pattern is observed for PtCtsEn (Fig. 2b) and CtsEn (Fig. 2c) samples, with a slight change in the temperature range at which the above changes occur. The substitution of phthaloyl and ethylene diamine groups appears to have enhanced the thermal stability of Cts, especially for the third stage of degradation.

3.4. Adsorption

The ability of material to capture the metal ions is governed mainly by the availability of functional groups which bind with metal ions and in some cases by the hydrophobility of the material (Arakaki et al., 2007; Machado, Da Fonseca, Arakaki, Espinola, & Oliveira, 2004). The ethylenediamine modified chitosan is expected to possess enhanced ability for binding metal ions due to the presence of a flexible ethylenediamine substituent with two nitrogen basic centres in addition to the $-NH_2$ at C-2 position. In PtCtsEn sample, the phthaloyl group renders the material more hydrophobic compared to CtsEn. In order to understand the effect of these

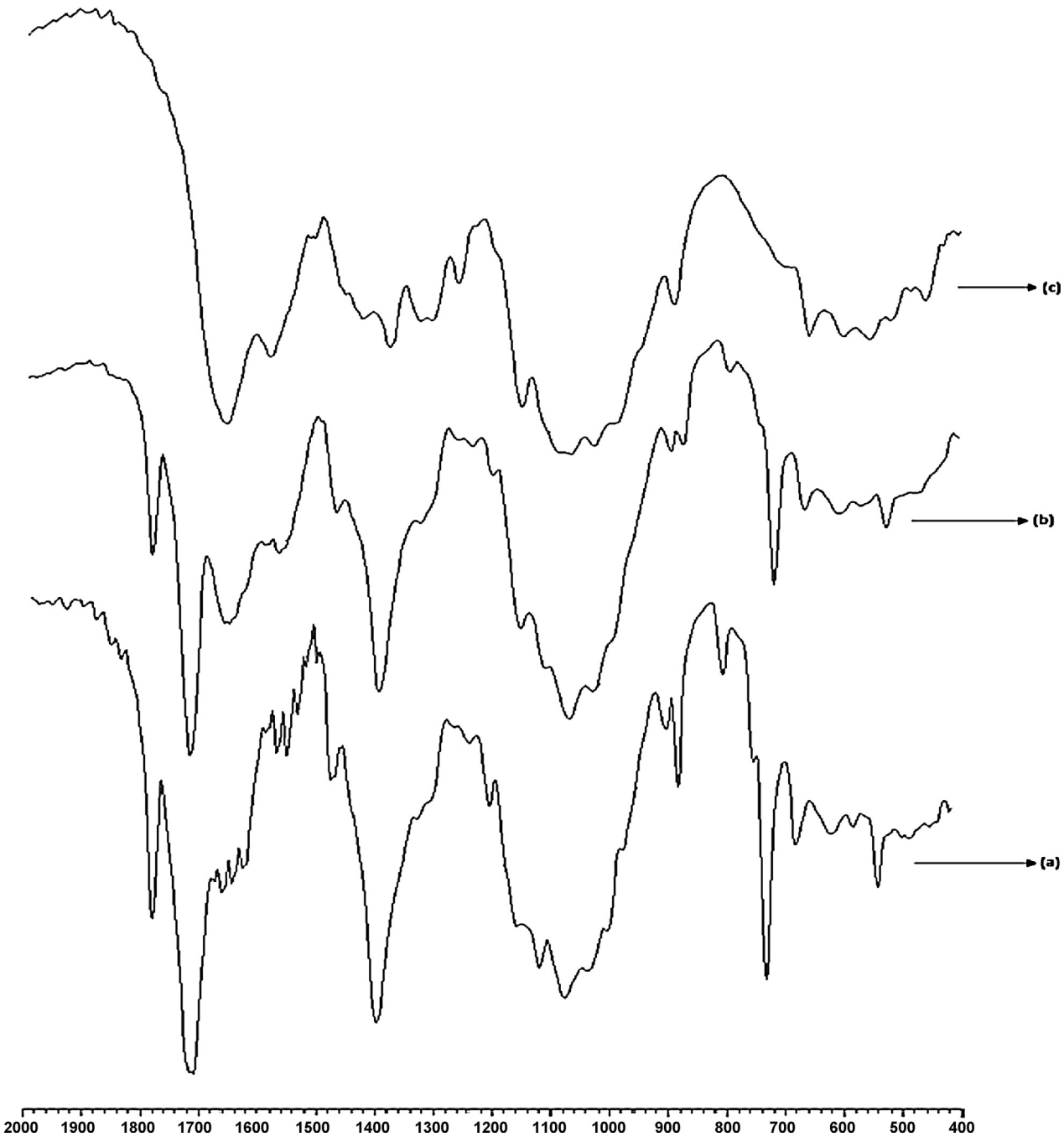


Fig. 1. FTIR spectra of (a) PtCtsCl, (b) PtCtsEn and (c) CtsEn.

substituents on efficacy of adsorption, the capacity of PtCtsEn and CtsEn to extract metal ions from aqueous solution was determined, in duplicate, by batch process, using divalent Cu, Zn and Pb salt solutions and compared with that of Cts and displayed in Fig. 3. Cts shows some tendency for adsorption of metal ions attributed to the presence of one nitrogen centre in each repeating unit. The incorporation of an additional nitrogen centre enhances the adsorption capacity appreciably as observed for PtCtsEn. Further improvement in the adsorption capacity is observed for the compound CtsEn due to the presence of three nitrogen centres. In comparison with Cts, the adsorption capacity of CtsEn is almost doubled, which is a significant improvement.

The Langmuir model which assumes monolayer formation on the adsorbent surface without any interaction between adsorbent molecules has been used in this study to determine the equilibrium between the adsorbent and the metal ions in adsorption medium.

The linearised form of the Langmuir equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max} K_L} + \frac{1}{q_{\max}} \tag{3}$$

where q_e and C_e are the amount adsorbed and the adsorbate concentration in solution, respectively, at equilibrium; K_L is the Langmuir constant and $q_{\max}$ is the maximum adsorption capacity when the monolayer is formed on the adsorbent.

The plots of C_e/q_e versus C_e obtained for the metal ion adsorption with CtsEn and PtCtsEn are shown in Fig. 4a and b, respectively. The values of Langmuir constants K_L and $q_{\max}$ obtained by the linear regression method are tabulated in Table 1.

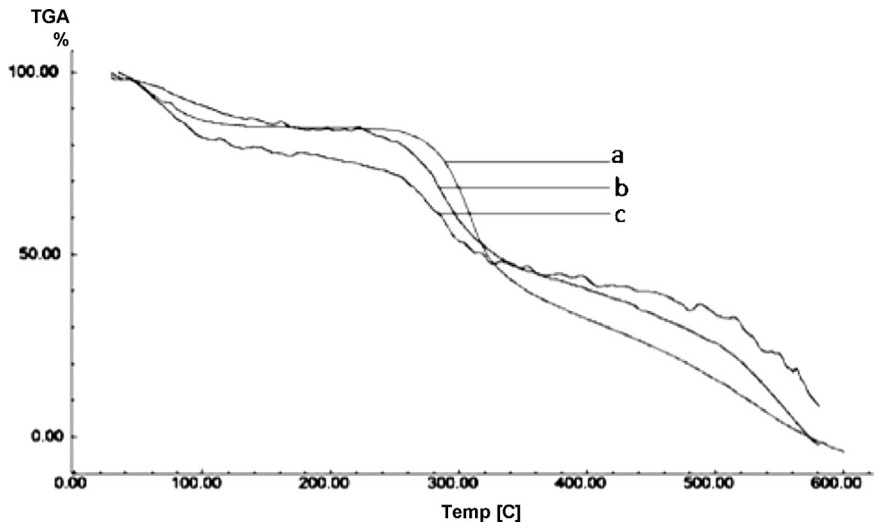


Fig. 2. TGA thermograms of (a) Cts, (b)PtCtsEn and (c) CtsEn.

Table 1
Langmuir constants for the adsorption of metal ions onto PtCtsEn and CtsEn (volume, 25 mL; adsorbent dose, 10 mg; initial concentration 5, 10, 15 and 20 ppm, contact time 1 h; temperature, 30 °C).

Metal	CtsEn				PtCtsEn			
	q_{max}	K_L	R_L	R^2	q_{max}	K_L	R_L	R^2
Cu(II)	41.6	4.8	0.023	0.999	32.3	3.875	0.026	0.999
Pb(II)	31.8	14.8	0.007	0.999	28.57	11.66	0.009	0.999
Zn(II)	20.0	12.5	0.008	0.999	18.6	4.815	0.020	0.999

Langmuir constant (K_L), maximum adsorption capacity (q_{max}), equilibrium parameter (R_L), and regression coefficient (R^2). R_L is calculated for initial concentration,10 ppm.

The high value of regression coefficient (R^2) indicates that the adsorption isotherms, in both cases, can be well described by the Langmuir model. The data further reveal that the q_{max} values obtained for the adsorption of all three metal ions are higher for CtsEn when compared to PtCtsEn. This is essentially due to the availability of one additional site, at C-2 position, for binding with metal ions in the former. The q_{max} data are in agreement with the establishment of the following order for adsorption on CtsEn and PtCtsEn; $Cu^{2+} > Pb^{2+} > Zn^{2+}$.

The equilibrium parameter (R_L) which is used to express the essential feature of Langmuir isotherm is given by Eq. (4).

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where C_0 is the initial metal concentration (mg L^{-1}). The R_L values indicate whether the adsorption is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Ngah et al., 2002; Laus & De Favere, 2011).

The values of R_L obtained in the present study are included in Table 1. The R_L values between zero and unity are indicative of favourable adsorption of metal ions on the two samples studied here.

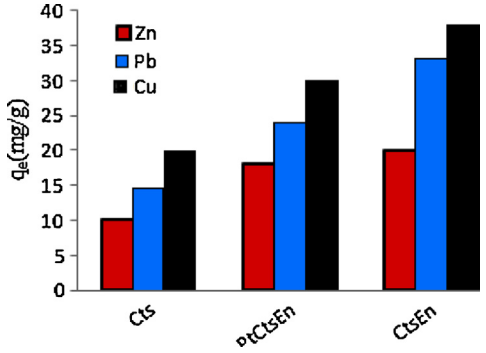


Fig. 3. Adsorption capacity of Cts, PtCtsEn and CtsEn for the three metal ions.

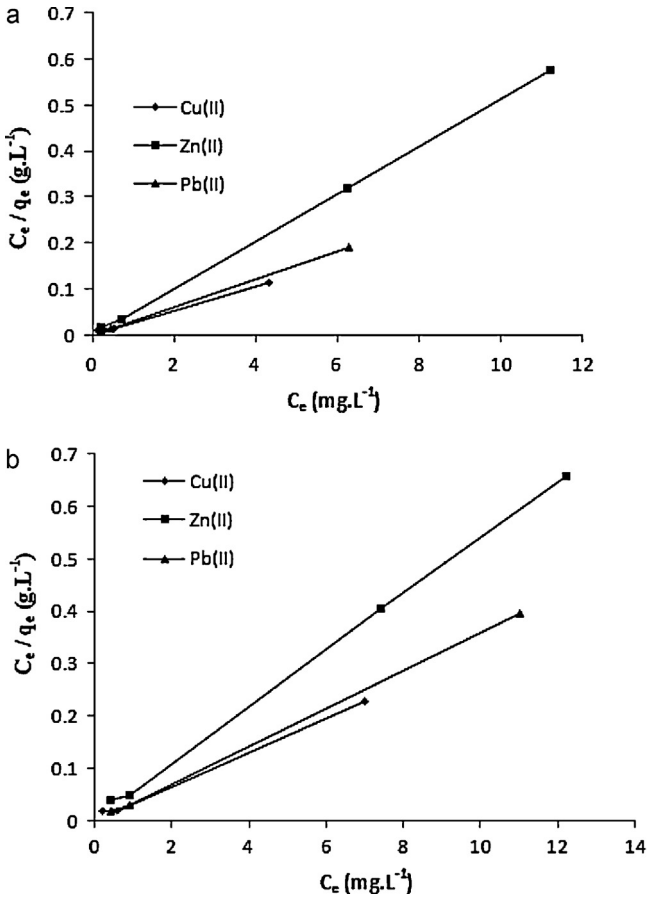


Fig. 4. (a) Langmuir isotherm for divalent metal ions on CtsEn. (b) Langmuir isotherm for divalent metal ions on PtCtsEn.

Table 2
Competitive adsorption for PtsCtsEn and CtsEn.

Metal	q_e (mg g^{-1})			
	CtsEn		PtCtsEn	
	Pure[a]	Mixed[b]	Pure[a]	Mixed[b]
Cu(II)	38.0	40.0	30.57	30.0
Pb(II)	30.57	25.0	24.40	12.9
Zn(II)	19.47	2.40	18.05	0.00

Equilibrium adsorption capacity (q_e).
[a] Adsorption experiments using solution of individual metal ion, 20 mg L^{-1}.
[b] Adsorption experiments using mixture of metal ions, each 20 mg L^{-1}.

3.5. Competitive adsorption of metal ions

The samples, CtsEn and PtCtsEn were evaluated for preferential adsorption of metal ions from a mixture containing the three metal ions under consideration. Table 2 shows the results of competitive adsorption. The preference for the three ions followed the order Cu > Pb > Zn, in both the adsorbent samples. The 'N' binding sites appear to have highest affinity for Cu and least for Zn among the three ions. Preferential adsorption of Cu over Pb has been reported in the literature for S-substituted cellulose derivatives (Aoki, Fukushima, Kurakata, Sakamoto, & Furuhata, 1999).

The total amount of metal ion adsorbed from the mixed solution exceeded the amount adsorbed from individual solutions. This may be due to the fact that different metal ions interacted with different types of binding sites. The synergistic effect, due to swelling state and conformation of adsorbent molecules, caused by the simultaneous sorption of several kinds of metal ions, has been proposed to be responsible for such enhanced sorption (Aoki et al., 1999).

3.6. Desorption studies

The desorption experiments were carried out with single metal (Cu/Zn) loaded samples. Aqueous salt solution of pH 1.2 was used as the stripping solution as the adsorbents have zero affinity for metal ions under acidic conditions. The results are shown in Fig. 5. It was observed that 92% of Cu and 97% of Zn was desorbed from loaded PtCtsEn whereas only 83% of Cu and 85% of Zn were desorbed from loaded CtsEn sample. These results showed that PtsCtsEn and CtsEn can be successfully regenerated by treatment with a solution of pH 1.2. At this pH, the amine nitrogens get protonated and lose their affinity for metal ions releasing the latter from the binding sites. The retention of about 15% of the adsorbed metal ions by CtsEn may be due to the inaccessibility of 'N' basic centres at C-2 position for protonation, due to the compact arrangements of chains involved in 'interchain' metal-adsorbent complex. The driving force governing adsorption of metal ions appears to be mainly the interaction between the metal cationic 'acidic' centre and 'basic' amine nitrogen centres. The lower adsorption and complete desorption in case of PtCtsEn indicate that hydrophobic forces do not contribute to adsorption process in the materials under consideration.

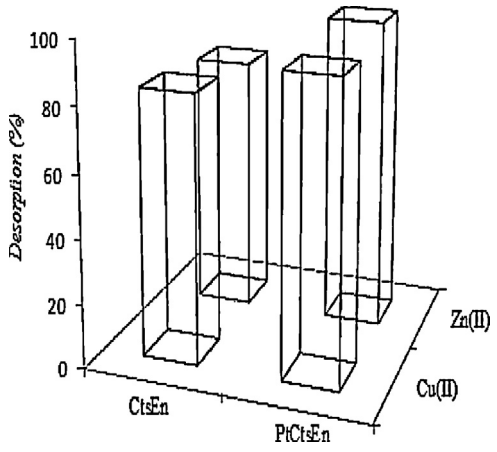


Fig. 5. Desorption of Cu and Zn ions from loaded CtsEn and PtCtsEn.

4. Summary

In the present study, selective modification of chitosan has been achieved by incorporating ethylene-1,2-diamine molecule in a highly regioselective manner using N-phthaloylchitosan and chloro-6-deoxy N-phthaloylchitosan as precursors. The present modification results in flexible pendant groups with additional basic nitrogen centres which function as potential binding sites during adsorption of metal cations. The parent compound, 'chitosan', the derivative 'ethylene-1,2-diamine-6-deoxy-chitosan' and its 'pthaloylated precursor' have been evaluated for divalent metal ion removal. The two derivatives are found to have higher capacity for adsorption of metal ions, compared to the parent, due to the presence of additional $-NH_2$ moiety. The analysis of adsorption data reveals homogeneous monolayer adsorption described well by Langmuir model. About 80% of the adsorbed metal ions could be stripped in aqueous salt solution of pH 1.2, proving the possibility of regeneration of original material. The interaction between acidic metal cation centres in solution and basic nitrogen centres on surface of adsorbent appears to be the major contributing factor governing adsorption. Both intrachain and interchain co-ordinate bonding involving $-NH$ and $-NH_2$ groups has been proposed to be the mechanism of formation of metal–adsorbent complex.

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