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Complexation of heavy metals by crosslinked chitin and its deacetylated derivatives

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Abstract

Chitin was crosslinked using diisocyanatohexane (HDI), trimellitic anhydride (TMA), and dibromodecane (DBD), then deacetylated in strong aqueous alkali. This led to a product with amine functional groups on the exposed surface of the crosslinked chitin, which could be utilized for complexation with heavy metals. Thus, a key feature of the crosslinked derivatives prepared was that only the hydroxy groups were utilized in the crosslinking reaction, and the acetylamino groups of chitin were hydrolyzed only after the crosslinking was accomplished. This ensured that all amino groups of the chitosans so produced would be available for metal complexation, and not partially used up in crosslinking. This proposed advantage was proved by the similar binding observed for heavy metals like Hg (348–372 mg/g), Cu (91–119 mg/g), Zn (71–92 mg/g), Mn (3–10 mg/g), Cd (121–160 mg/g), and Pb (32–86 mg/g) using these crosslinked polymers, whereas the control polymer (uncrosslinked chitosan powder) had complexation values for Hg (348–361 mg/g), Cu (100–106 mg/g), Zn (81–92 mg/g), Mn (4–7 mg/g), Cd (135 mg/g), and Pb (25–59 mg/g). Additionally, in a case where chitosan was crosslinked with HDI, the amino groups were consumed in the crosslinking reaction, and the metal complexation capacity has found to be decreased for Cu (91–109 mg/g), Cd (133 mg/g), and Zn (71–77 mg/g), while remaining nearly the same for Hg (362 mg/g). The literature value for Cu complexation is 59.67 mg/g for chitosan crosslinked with glutaraldehyde. The crosslinked derivatives have the added advantage of insolubility even in low pH aqueous media, making their repeated re-use possible. Further, these crosslinked derivatives could be used in powder form, and the additional step of preparing beads was found to be not necessary for ease of separation of the crosslinked powder by filtration. The binding capacity of various crosslinked chitin and deacetylated derivatives for Cu, Cd, Hg, Zn, Mn, and Pb was in the region of 100, 140, 360, 88, 5, and 60 mg/g (rounded off values) of polymer, respectively, very close to the values obtained for uncrosslinked chitosan. The metal binding for crosslinked chitosan was slightly lower than that of crosslinked chitin and deacetylated derivatives, due to use of some amino groups in crosslinking. For Cu ions, the Langmuir equation was found to be the best fit for HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin. The morphological studies conducted using WAX-RD are in close agreement with the metal complexation data, showing complete loss of original chitosan peaks for the heavily complexed derivatives, and minor changes for the weakly complexed metals.

Keywords: Chitosan; Crosslinked chitosan; Deacetylated chitin; Metal complexation; Morphology

1. Introduction

A key property of soluble polymers endowed with functional groups is their ability to complex with a variety of metal ions in solution. For water soluble polysaccharides, the optimum binding of a particular metal to a particular polymer having suitable ligands (such as carboxyl or amino groups) occurs under specific conditions of pH, polymer concentration, metal concentration, temperature, and so on. However, crosslinked polymers offer flexibility in metal binding conditions, as polymer solubility, conformation, molecular weight, and concentration is not an issue. Here, the surface area, concentration of metal complexing ligands on the surface of the crosslinked polymer and porosity of

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the crosslinked polymer will affect the extent of binding. A very large number of publications have dwelt on the complexation ability of chitosan and its crosslinked derivatives with complex transition metals, organic species like dyes, and enzymes (Bassi, Prasher, & Simpson, 2000; Dobetti & Delben, 1992; Domard & Piron, 2000; Juang, Wu, & Tseng, 2002; Li, Chen, & Liu, 2003; Merrifield, Davids, MacRae, & Amirbahman, 2004; Rhazi et al., 2002; Schmuhl, Krieg, & Keizer, 2001; Taboada, Cabrera, & Cardenas, 2003; Tan, Wang, Peng, & Tang, 1999; Varma, Deshpande, & Kennedy, 2004). However, we believe this to be the first study where chitin was first crosslinked and then deacetylated to give crosslinked chitosans which have been used here to study heavy metal complexation without bead formation. Results of crosslinked chitosans with these new structures and morphologies will help in gaining new insights into factors affecting metal binding to chitosans. A recent study on glutaraldehyde crosslinked chitosan (Webster, Halling, & Grant, 2007) infers that though the surface area of the crosslinked polymer increases, the effect of crosslinking is to increase the competition of metal-binding *N* sites, which in turn decreases the metal uptake. Using our methodology, the crosslinked polymer does not exhibit decrease in metal uptake. Another recent paper (Kopecky, Kopecka, & Misikova, 2005) showed the importance of the counterion in metal complexation, where the changes for Cu can range from 140 mg/g for $Cu(NO_3)_2$ to 190 mg/g for $CuSO_4$. However, this aspect was not investigated in the present research.

Investigations on many other materials like fly ash, silica gel, zeolites, lignin, seaweed, wool wastes, agricultural wastes, clay materials, sugarcane bagasse, etc., have also been reported for applications like the removal of pollutants from aqueous streams, especially for heavy metals like Cd^{2+}, Cr^{3+}, Cr^{6+}, Hg^{2+}, and Pb^{2+} (Varma et al., 2004). A search of the published literature shows that maximum adsorption capacities for complexing Cd^{2+}, Cr^{3+}, and $Hg^{2+}$are 558, 92, 1123 mg/g of chitosan, respectively, which are higher than that of other polysaccharide materials studied (Bailey, Olin, Bricka, & Adrian, 1999). For example, sugarcane bagasse and its oxidized product (Filho, Winkler, Hechenleitner, & Gomez-Pineda, 1996) can bind Cu^{2+}; the adsorption capacity being 0.1292 mmol/g (8.21 mg/g), while the value for chitosan beads is 80.71 mg/g and 59.67 mg/g for chitosan crosslinked with glutaraldehyde (Ngah Wan, Endud, & Mayanar, 2002). Similarly, lignin from bagasse can bind Cd^{2+} and Pb^{2+} (Peternele, Winkler-Hechenleitner, & Gomez-Pineda, 1999). Analysis of these studies make it clear that chitosan and its crosslinked derivatives have greater capacity for complexing heavy metals, and are also amenable to easy functionalization by specific ligands for building specificity into the molecule.

In this present study, the complexation of a series of heavy metal salts of Cu^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+} to a series of crosslinked chitosans were investigated by a variety of techniques like UV spectroscopy, wet chemical methods (appropriate titration methods for each case), atomic absorption spectroscopy, langmuir adsorption studies, and wide angle X-ray diffractometry. Evidence for specific as well as non-specific interaction between the metal ion and the polymer could be detected. The ligands on the crosslinked polymers were predominantly amino groups, along with hydroxyl groups (and, in the case of trimellitic anhydride crosslinking, some carboxyl groups were also present). All the chosen heavy metals have implications in toxic interactions in living systems, in addition to industrial applications like ion-exchange media and pollution control. This comprehensive investigation seeks to simplify the metal complexation methodology and obtain an understanding of the morphology of the metal complexes.

2. Experimental

2.1. Materials

The chitin and chitosan used in this study are commercial products of Meron Biopolymers, Cochin, Kerala, India. (^{13}C-CPMAS NMR are shown in Fig.1(1) and (2)). D-glucosamine was obtained from Sigma Chemical Co. (St. Louis, MO). Diisocyanatohexane (HDI) was obtained from Aldrich Chemical Co., trimellitic anhydride (TMA) and dibromodecane (DBD) was obtained from Merck. Dimethylformamide, toluene, and sodium hydroxide pellets were AR grade chemicals, obtained from SD fine chemicals, Mumbai. Sodium hydride was obtained from Merck. 4-Dimethylaminopyridine was purchased from Lancaster Company. All metal salts were AR grade materials and used without further purification. The salts $ZnCl_2$, $MnSO_4$, $CdSO_4$, $Pb(NO_3)_2$ were obtained from Loba Chemie, Mumbai, $CuSO_4$ was from SD Fine Chemicals, Mumbai, and $HgCl_2$ was from Merck.

2.2. Synthetic procedures

2.2.1. General procedure for deacetylation of chitin and crosslinked chitin

Ten grams of chitosan was dispersed in 200 ml of 50% NaOH solution (100 g NaOH dissolved in 153 ml distilled water). The reaction was carried out in a high pressure Parr reactor by first bubbling in nitrogen gas through the reaction mixture for 5 min, followed by maintaining nitrogen gas pressure of 60 psi in the reactor. The temperature was set at 135 °C and maintained at 135 °C for 3.5 h, with stirring at 200 rpm. Under these conditions, the gage pressure reading was 100 psi. The whole reaction mixture was transferred into 4 L of distilled water and left as such for 2 h. Then the water layer was decanted and the solid separated was washed with distilled water and methanol till the pH of the wash water was neutral. Finally solid was washed with methanol and dried under vacuum. Fig. 1(3) shows the ^{13}C-CPMAS NMR of deacetylated chitin.

Calculations for the degree of deacetylation. Degree of acetylation (DA) and degree of deacetylation (DD) calcu-

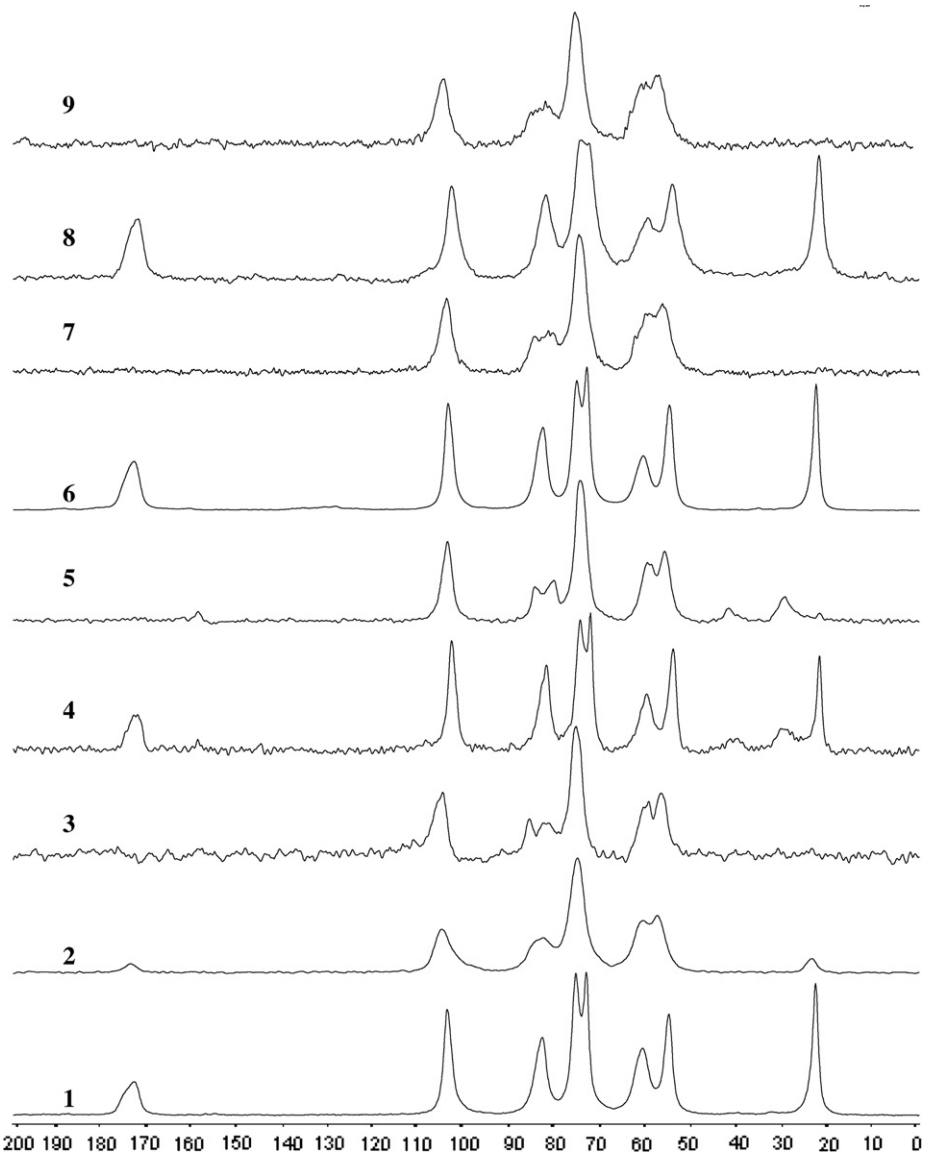

Fig. 1. CPMAS ^{13}C NMR of (1) chitin (Meron), (2) commercial chitosan (Meron), (3) deacetylated chitin (chitosan), (4) HDI crosslinked chitin, (5) HDI crosslinked deacetylated chitin (chitosan), (6) TMA crosslinked chitin, (7) TMA crosslinked deacetylated chitin (chitosan), (8) DBD crosslinked chitin, (9) DBD crosslinked deacetylated chitin (chitosan).

lated from ^{13}C CP/MAS NMR spectroscopy (*Journal of Applied Polymer Science, 93*, 1876–1885 (2004))

$$\mathrm{DA}\% = \frac{I_{\mathrm{CH_3}}}{(I_{\mathrm{C1}} + I_{\mathrm{C2}} + I_{\mathrm{C3}} + I_{\mathrm{C4}} + I_{\mathrm{C5}} + I_{\mathrm{C6}})/6} \times 100$$

$$\mathrm{DD}\% = 100 - \mathrm{DA}$$

By this method, the degree of deacetylation of chitin to produce chitosan using the above deacetylation procedure was 88%. By this same procedure we calculated the degree of deacetylation of commercial chitosan (obtained from Meron, India) as 85%.

2.2.2. Diisocyanatohexane-crosslinked deacetylated chitin

Forty grams (0.1970 M) of dry chitin was stirred in dry and distilled toluene (300 ml) and shaken well. It was left for 2 h at room temperature. It was filtered to obtain moisture free chitin. This moisture free chitin was dispersed in 500 ml dry distilled toluene in a round bottom flask equipped with reflux condenser and calcium guard tube. It was stirred vigorously at 50 °C using a mechanical stirrer. 35 ml (0.2167 M) diisocyanatohexane (HDI) diluted in 100 ml dry distilled toluene was added dropwise over a period of one hour at 50 °C. After completion of addition, the reaction was continued at 50 °C for 5 h.

The reaction mixture was then filtered. The solid part was washed with toluene two to three times and finally dried. Fig. 1(4) shows the ^{13}C-CPMAS NMR of HDI crosslinked chitin.

Deacetylation of HDI-crosslinked chitin. Ten grams of HDI-crosslinked chitin was deacetylated by the above mentioned deacetylation procedure. The weight of the

deacetylated product was 8.6 g. The CPMAS ^{13}C NMR is shown in Fig. 1(5).

2.2.3. Trimellitic anhydride-crosslinked deacetylated chitin

Twenty grams (0.0985 M) of dry chitin was dispersed in dry and distilled DMF (150 ml) and shaken well. It was left for 2 h at room temperature. It was filtered to obtain moisture free chitin. This moisture free chitin was dispersed in 300 ml dry distilled DMF taken in round bottom flask equipped with a reflux condenser and guard tube. It was stirred vigorously at 110 °C using a mechanical stirrer. 200 mg of DMAP was added in the reaction flask and 4 g (0.0202 M) trimellitic anhydride (TMA) diluted in 20 ml dry distilled DMF was added dropwise over a period of 40 min at temperature 110 °C. Reaction was continued at 110 °C for 6 h. The reaction mixture was filtered and the solid was separated and washed with methanol several times and finally dried. The CPMAS ^{13}C NMR is shown in Fig. 1(6).

Deacetylation of trimellitic anhydride-crosslinked chitin. Trimellitic anhydride-crosslinked chitin (10 g) was deacetylated by the general procedure outlined earlier. Weight of the TMA-crosslinked deacetylated chitin obtained was 6.85 g. The CPMAS ^{13}C NMR is shown in Fig. 1(7).

2.2.4. Dibromodecane-crosslinked chitin

Forty grams (0.1970 M) of dry chitin was dispersed in 300 ml dry distilled DMF taken in a round bottom flask and shaken well. It was left overnight at room temperature. It was filtered to obtain moisture free chitin. This moisture free chitin was dispersed in 500 ml dry distilled DMF taken in a round bottom flask equipped with a reflux condenser and calcium guard tube. It was stirred vigorously at room temperature using a mechanical stirrer. Ten milliliters (13.35 g) (0.0445 M) of 1,10-dibromodecane was added dropwise at room temperature. Then slowly increase the temperature to 110 °C. Then added portion wise 2.2 g (0.092) of NaH (3.7 g of 60% dispersion of NaH in mineral oil). At that time, maintain the temperature at 110 °C. Complete addition of NaH took 6 h. After completion of addition, the reaction was continued at 110 °C for 1 h.

The reaction mixture was filtered. The solid was washed with distilled water to remove NaBr. The solid was washed with distilled water till the filtrate shows neutral and finally solid washed with acetone and dried. The CPMAS ^{13}C NMR is shown in Fig. 1(8).

Deacetylation of dibromodecane-crosslinked chitin. Dibromodecane-crosslinked chitin (10 g) was deacetylated by the general deacetylated procedure outlined earlier. Weight of the dibromodecane-crosslinked deacetylated chitin obtained was 7.25 g. The CPMAS ^{13}C NMR is shown in Fig. 1(9).

2.2.5. Diisocyanatohexane-crosslinked chitosan

Forty grams (0.1970 M) of dry chitosan was dispersed in dry and distilled toluene (300 ml) taken in round bottom flask and shaken well. It was left for 2 h at room temperature. It was filtered to obtain moisture free chitosan. This moisture free chitosan was dispersed in dry distilled toluene (500 ml) taken in a round bottom flask equipped with a reflux condenser and calcium guard tube. It was stirred vigorously at 50 °C using a mechanical stirrer. Diisocyanatohexane (HDI) (35 ml (0.2167 M)) diluted in 100 ml dry distilled toluene was added dropwise over a period of 1 h at 50 °C. Reaction was continued at 50 °C for 5 h. The reaction mixture was filtered and the solid separated. The solid was washed with toluene two to three times and finally dried.

2.3. Methods for evaluation of metal complexation

2.3.1. Determination of the metal complexation capacity by titration method

Chitosan and crosslinked derivatives prepared as above (approximately 100 mg) were dispersed in 20 ml of 0.01 M metal solutions (e.g., $CuSO_4{\cdot}5H_2O$, $MnSO_4{\cdot}H_2O$, $ZnSO_4{\cdot}H_2O$, $CdSO_4{\cdot}8/3H_2O$, $Pb(NO_3)_2$, $HgCl_2$) and were shaken at 90 rpm in a lab shaker bath overnight at room temperature. After that it was filtered, and the filtrate was used for titration as well as UV study and AAS study.

Determination of copper complexation. Ten milliliters of filtrate was taken in a conical flask and diluted with 40 ml deionized water. Adjust the pH of the solution to 10–11 by the addition of 1 ml of 25% aqueous ammonia solution. Add few drops of fast sulphon black F as an indicator and titrate against 0.01 M EDTA solutions until the color changes from purple to green. For blank titration use 0.01 M $CuSO_4{\cdot}5H_2O$ solution instead of filtrate.

Determination of zinc complexation. Ten milliliters of filtrate was taken in a conical flask and diluted with 40 ml deionized water. Adjust the pH of the solution to 10 by the addition of 4 ml of ammonia and ammonium chloride buffer solution (pH is approximately 10). Add few drops of solochrome black T as an indicator and titrate against 0.01 M EDTA solutions until the color changes from purple to light green color. For blank titration use 0.01 M $ZnSO_4$ solution instead of filtrate.

Determination of manganese complexation. Ten milliliters of filtrate was taken in a conical flask and diluted with 40 ml deionized water, then add 0.1 g ammonium hydroxide hydrochloride and 1.5 ml triethanol amine. Adjust the pH of the solution to 10 by the addition of 4 ml of ammonia and ammonium chloride buffer solution (pH is approximately10). Add few drops of solochrome black T as an indicator. Titrated it against 0.01 M EDTA solutions until the color changes from purple to bluish green color. For blank titration use 0.01 M $MnSO_4$ solution instead of filtrate.

Determination of lead complexation. Ten milliliters of filtrate was taken in a conical flask and diluted with 40 ml deionized water. Adjust the pH of the solution to 6 by the addition of 4 ml of 30% aqueous hexamine buffer solution (pH is 6–7). Add few drops of 0.2% aqueous xylenol orange as an indicator. Titrated it against 0.01 M EDTA

solutions until the color changes from purple to light yellow color. For blank titration use 0.01 M $Pb(NO_3)_2$ solution instead of filtrate.

Determination of mercury complexation. Ten milliliters of filtrate was taken in a conical flask and diluted with 40 ml deionized water. Adjust the pH of the solution to 6 by the addition of 4 ml of 30% hexamine buffer solution (pH is 7–8). Add few drops of methyl thymol blue as an indicator. Titrate it against 0.01 M EDTA solutions until the color changes from light purple to t yellow color by literature it was blue to yellow color. For blank titration use 0.01 M $HgCl_2$ solution instead of filtrate.

Determination of cadmium complexation. Ten milliliters of filtrate was taken in a conical flask and diluted with 40 ml deionized water. Adjust the pH of the solution to 5 by the addition of 4 ml of 30% hexamine buffer solution (pH is 6–7). Add few drops of 0.2% xylenol orange as an indicator and titrate against 0.01 M EDTA solutions until the color changes from light purple to yellow color by literature it was blue to yellow color. For blank titration use 0.01 M $CdSO_4{\cdot}8/3H_2O$ solution instead of filtrate.

2.3.2. Metal adsorption capacity by UV spectrophotometry

The filtrates from above Section 2.3 were used for calculating the value of absorbance from the standard calibration curves generated earlier. Results are reported in Table 1.

2.3.3. By Atomic Absorption spectrophotometer

The filtrates from above Section 2.3 were used for calculating the concentration of the metal ion in mg/l in the solution, after preparing standard calibration curves. Results are reported in Table 1.

2.4. Adsorption experiments

Langmuir and Freundlich adsorption equilibrium studies were conducted for the specific case of copper ion complexation using diisocyanatohexane-crosslinked deacetylated chitin and trimellitic anhydride-crosslinked deacetylated chitin powder. The isotherm studies were conducted with a constant weight of crosslinked deacetylated chitin powder weight (100 mg) and adding varying initial concentration of Cu(II) ions in the range 125–2500 ppm in aqueous media, with contact time of 24 h and pH 7.0.

Langmuir adsorption. The extent of adsorption was calculated based on the difference of Cu(II) concentration in the aqueous solution before and after adsorption, as follows (Atia, Ahmed, & Elwakeel, 2005)

$$\text{Adsorption capacity } (X) = \frac{(C_o - C_e)}{W} V$$

where C_o is the initial Cu(II) concentration (ppm), C_e is the final or equilibrium concentration (ppm), V is the volume of Cu(II) solution (in liters), and W is the weight of the crosslinked deacetylated chitin powder (g).

The basic assumption in Langmuir adsorption isotherm is that the adsorbed layer is one molecule thick and that all sites are equal, thereby resulting in equal energies and enthalpies of adsorption (Ngah Wan & Musa, 1998). The strength of the intermolecular attractive forces is believed to fall of rapidly with distance. The sorption data were analyzed according to the linear form of the Langmuir isotherm

$$C_e/X = C_e/X_{max} + 1/X_{max}b$$

where C_e is the equilibrium or final concentration of M(II) (ppm), X is the amount of M(II) adsorbed per unit weight of chitosan at equilibrium concentration (mg/g), X_{max} is the maximum adsorption at monolayer coverage (mg/g) and b is the Langmuir adsorption equilibrium constant (ml/mg) and is a measure of the energy of adsorption. Figs. 2 and 3 show the experimental equilibrium isotherms for adsorption of M on HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin.

Uptake measurements. Uptake experiments of the Cu(II) ions were done by placing 100 mg of dry HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin in a series of flasks containing 20 ml Cu(II) solution in the concentration range 125–2500 ppm. The flasks were kept at room temperature with shaking over a period of 24 h. After the completion of equilibration time solution was filtered and 10 ml of filtrate was titrated against 0.01 M EDTA using fast sulphon black F as indicator.

From Fig. 2, it is seen that the adsorption capacity of HDI-crosslinked deacetylated chitin and TMA-crosslinked

Table 1
Removal of heavy metal by chitosan and crosslinked chitosan for metal ion solutions (mg/g)

Sample name	Cu^{2+} (mg/g)		Cd^{2+} (mg/g)		Hg^{2+} (mg/g)		Zn^{2+} (mg/g)		Mn^{2+} (mg/g)		Pb^{2+} (mg/g)	
	Titrn.	UV AAS	Titrn.	UV AAS	Titrn.	UV AAS	Titrn.	UV AAS	Titrn.	UV AAS	Titrn.	UV AAS
Chitosan (Meron)	100	104 106	135	a b	348	361 b	92	a 81	07	a 04	59	25 46
Deacetylated chitin	107	111 119	121	a b	356	372 b	88	a 73	05	a 04	53	65 33
HDI-crosslinked deacetylated chitin	103	107 115	145	a b	348	370 b	85	a 77	05	a 08	55	49 33
Dibromodecane-crosslinked deacetylated chitin	104	104 115	160	a b	361	362 b	87	a 79	06	a 04	51	32 33
Trimellitic anhydride-crosslinked deacetylated chitin	100	111 116	134	a b	360	361 b	90	a 84	03	a 10	69	82 33
HDI-crosslinked chitosan	091	099 109	133	a b	362	362 b	77	a 71	05	a 06	67	86 33

Titrn., by titration method; UV, by Ultraviolet spectrophotometer method; AAS, by Atomic Absorption spectrophotometer method; a, λ_{max} shows below 190 nm; b, due to unavailability of particular metal lamp.

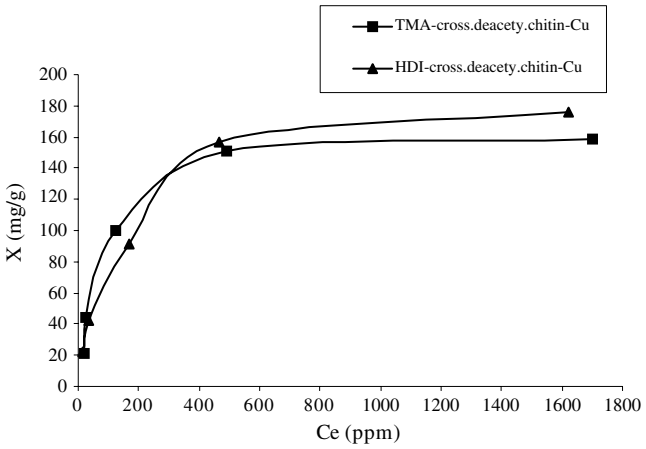

Fig. 2. Adsorption isotherm of Cu(II) ion on HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin

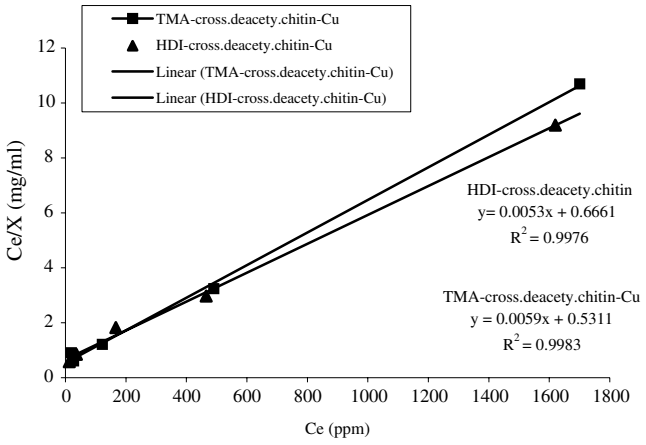

Fig. 3. Adsorption isotherms of Cu(II) by the HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin, linearized according to the Langmuir isotherm.

Table 2
Uptake capacity or adsorption capacity (X) (mg/g) of HDI-crosslinked deacetylated chitin and TMA-crosslinked deacetylated chitin using Cu(II) towards different initial concentrations

Initial concentration (C_e) (ppm)	Uptake capacity or adsorption capacity (X) (mg/g)	
	HDI-crosslinked deacetylated chitin	TMA-crosslinked deacetylated chitin
2500	176.1	159.12
1250	156.38	151.42
625	91.37	100.24
250	42.37	44.39
125	22.32	21.09

deacetylated chitin increases as the concentration of Cu(II) ion increases until an equilibrium concentration of about 490 ppm.

From Table 2 it is seen that the maximum uptake capacity of HDI-crosslinked deacetylated chitin–Cu(II) was 176.1 mg/g and TMA-crosslinked deacetylated chitin–Cu(II) was 159.12 mg/g. These are much higher than the values reported by other workers, such as 59.67 mg/g for chitosan crosslinked with glutaraldehyde (Ngah Wan et al., 2002).

Uptake capacity increases with the increase of equilibrium concentration until reaching a saturation value 156.38 mg/g for HDI-crosslinked deacetylated chitin–Cu(II) and 151.42 mg/g for TMA-crosslinked deacetylated chitin–Cu(II) after that concentration has no longer effect on uptake capacity.

Plotting the graph of C_e versus C_e/X gives X_{max} and b (Fig. 3) shows that the experimental adsorption isotherm values are fitted into the linearized forms of the Langmuir equation (correlation coefficient was found to be $R^2 > 0.99$). From the slope and the intercept of the straight lines the numerical values of Langmuir constants were obtained are shown in Table 3.

Freundlich isotherm. The Freundlich isotherm is another form of the Langmuir approach used for studying adsorption on amorphous surfaces (Ng, Cheung, & Mckay, 2002). The Freundlich equation shows that the metal concentrations on the adsorbent will increase as long as there is an increase in the metal ions concentrations in the solution. The equation can be represented by

$$X = K_F C_e^{b_F}$$

where $b_F = 1/n$, K_F is the Freundlich constant and represents the adsorption capacity (mg/g), b_F is the Freundlich exponent, and "n" is a constant which represents adsorption intensity (see Table 4).

If it is in the linear form of the Freundlich equation, it will yield the constants K_F and b_F. In this case, $\text{Log}\, X = 1/n \log C_e + \log K_F$.

Fig. 4 shows the adsorption isotherm of Cu(II) ion with HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin on the linearized form of Freudlich

Table 3
Experimental Langmuir isotherm constants and correlation coefficients

Sample used	Metal ion	Adsorption constant		R^2
		X_{max}	b (L/mmol)	
HDI-crosslinked deacetylated chitin	Cu(II)	188.67	0.008	0.9976
TMA-crosslinked deacetylated chitin	Cu(II)	169.49	0.011	0.9983

Table 4
Freundlich isotherm constant for Cu(II) ion sorption onto HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin

Sample–Cu(II)	$1/n = b_F$ (mg/g)	K_F (dm^3/g)	R^2
HDI-crosslinked deacetylated chitin–Cu(II)	0.4457	8.2281	0.9566
TMA-crosslinked deacetylated chitin–Cu(II)	0.422	9.2512	0.8495

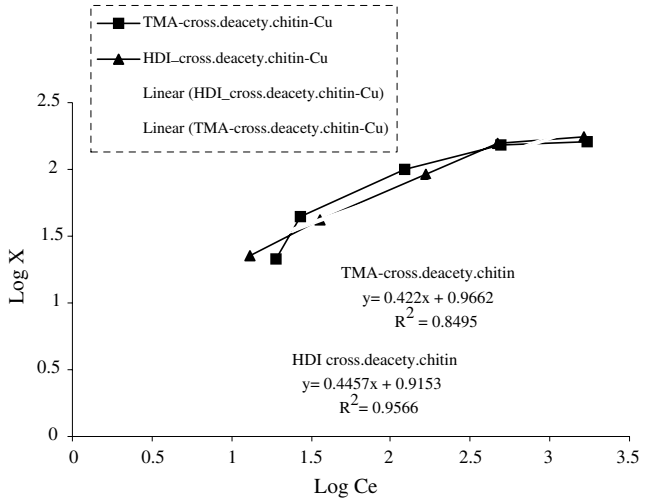

Fig. 4. Adsorption isotherm of Cu(II) ion with HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin on the linearized form of Freudlich equation.

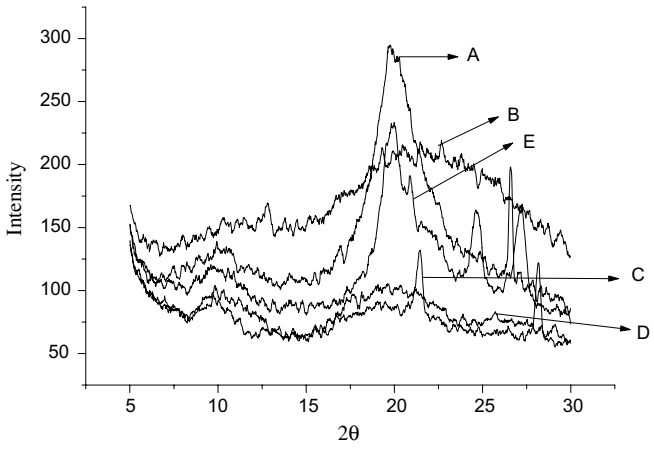

Fig. 5. WAXRD of (A) chitosan, (B) chitosan–Cu complex, (C) chitosan–Hg complex, (D) chitosan–Cd complex, (E) chitosan–Pb complex.

equation. The graph is linear for the HDI crosslinked material, but not so with the TMA crosslinked material.

Wide-angle X-ray diffraction. From Fig. 5(A) it is seen that chitosan shows three characteristic peaks of crystalline nature at 9.85°, 19.70°, and 26.57° but the chitosan–Cu complex (Fig. 5(B)) is characterized by a broad amorphous peak at 22.16. A similar spectrum has been reported earlier (Yin et al., 2004). Thus, complexation of Cu(II) leads to very significant changes in the morphology of the chitosan, indicating complete disruption of the interpolymer bonds.

Similarly, the chitosan–Hg complex (Fig. 5(C)) shows three peaks of crystalline region at 9.76°, 21.50°, and 28.17°. From the literature, $HgCl_2$ shows three characteristic peaks of crystalline region at 20.40°, 29.46°, and 21.66°. The main chitosan peak characteristic of chitosan disappears in chitosan–Hg complex due to disruption of the interpolymer bonds.

In the case of chitosan–Cd complex (Fig. 5(D)), one characteristic peak of crystalline region at 9.83° of chitosan is observed, while the major characteristic peaks of chitosan as well as $CdSO_4{\cdot}H_2O$ disappear. This is reflected in the lower extent of Cd complexation to chitosan as compared to Cu and Hg.

In Fig. 5(E), the very small extent of complexation of Pb with chitosan is further proved by the negligible change in the WAXRD spectrum.

Exactly the same WAXRD results were obtained with TMA-crosslinked deacetylated chitin, and are therefore not reproduced here.

3. Conclusions

The studies carried out indicate that simple crosslinking of chitin with crosslinking agents like HDI, TMA, and DBD followed by deacetylation affords a simple method of obtaining a resin with amino groups at the surface which give high degrees of complexation with heavy metals like Cu and Hg, comparable to the highest values reported in literature for chitosans, crosslinked chitosans, and chitosan beads. For binding of copper ions, we found the Langmuir equation to be the best fit for HDI crosslinked deacetylated chitin and TMA crosslinked deacetylated chitin. The morphology of the metal complexes was studied in a facile manner by WAXRD, which afforded an easy tool to evaluate the extent of binding. Thus, high values of metal complexation lead to WAXRD spectra where the original chitosan peaks substantially disappear. Thus a study of WAXRD is in itself a powerful tool to study the extent of metal binding by polymer ligands where the key functional groups are extensively utilized in binding, thereby disrupting the original polymer structure and the consequent changes in the WAXRD spectra. Weak complexes like that of Pb do not lead to any changes in the WAXRD spectra.

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