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Short communication

A morphological study of heavy metal complexes of chitosan and crosslinked chitosans by SEM and WAXRD

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Abstract

Metal complexes of salts of Hg, Cu, Cd, Pb, Zn, and Mn with chitosan and crosslinked chitosans were prepared, and their morphologies were studied using scanning electron microscopy and wide angle X-ray diffraction. The metal ions which were specifically and strongly complexed to the amino functions of chitosans, like Hg, showed smooth surface morphology inspite of large number of ions complexed (372 mg/g of chitosan). The presence of metal ions on the surface of the chitosans could be detected with decrease in metal ion binding, in the following sequence Hg > Cu > Cd > Zn > Pb > Mn. Particularly in the case of Pb ions, the presence of these ions is clearly seen on the surface of the polymer by SEM. The number of ions of Mn complexed on the polymers was too few (5 mg/g of chitosan) to be visible. SEM of Hg and Cu complexes do not show the "holes" observed in the crosslinked polymers as they bind specifically to amino groups of chitosan, but for Cd, Zn, Mn, and Pb complexes, these "holes" are clearly visible. These results are also in agreement with the morphologies studied by WAXRD. The metal complexation data for each of these metal ions was also in the same sequence.

Keywords: Morphology; Metal complex; Chitosan; Crosslinked chitosan; SEM; WAXRD

1. Introduction

One of the key properties of chitosan is its ability to complex strongly with heavy metal ions, especially with Hg, Cu, Pb, Zn, Ni, Cr, and so on, and several applications proposed are in water purification for removing toxic metals by complexation (Bailey, Olin, Bricka, & Adrian, 1999; Elson, Davies, & Hayes, 1980; Muzzarelli & Rocchetti, 1974; Varma, Deshpande, & Kennedy, 2004) Further, crosslinked polymers offer flexibility in metal binding conditions, as polymer solubility, conformation, molecular weight, and concentration are not an issue. Here, the surface area and surface morphology, concentration of metal complexing ligands on the surface of the crosslinked polymer and porosity of the crosslinked polymer will affect the extent of binding. Recently we reported (Trimukhe & Varma, 2008) our detailed investigation into the heavy metal ion binding (Hg, Cu, Cd, Pb, Zn, Mn) to a series of crosslinked chitosans, using trimelitic anhydride, diisocyanatohexane, and dibromodecane as crosslinking agents. This is the first study wherein chitin was first crosslinked and then deacetylated to give crosslinked chitosans retaining all the amino groups, which are crucial functional groups for specific heavy metal ion complexation. The present study reports the morphologies of the metal complexes obtained. Results of crosslinked chitosans with these new structures and morphologies will help in gaining new insights into factors affecting metal binding to chitosans.

2. Experimental section

2.1. Materials

The chitin and chitosan used in this study are commercial products of Meron Biopolymers, Cochin, Kerala, India. Diisocyanatohexane (HDI) was obtained from

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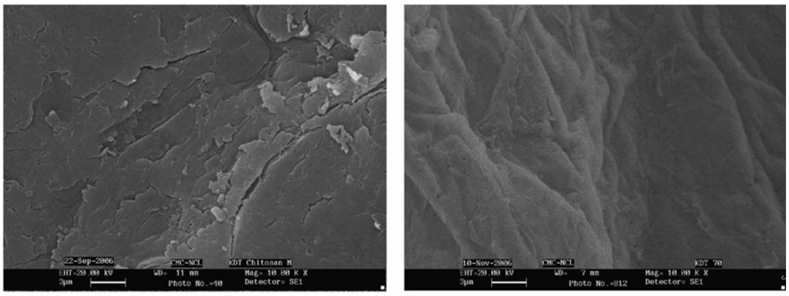
Aldrich Chemical Co., trimellitic anhydride (TMA) and dibromodecane (DBD) were obtained from Merck. Dimethylformamide, toluene, and sodium hydroxide pellets were AR grade chemicals, obtained from SD Fine Chemicals, Mumbai. Sodium hydride was obtained from Merck. 4-Dimethylaminopyridine was purchased 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

These are reported in detail in a previous publication (Trimukhe & Varma, 2008).

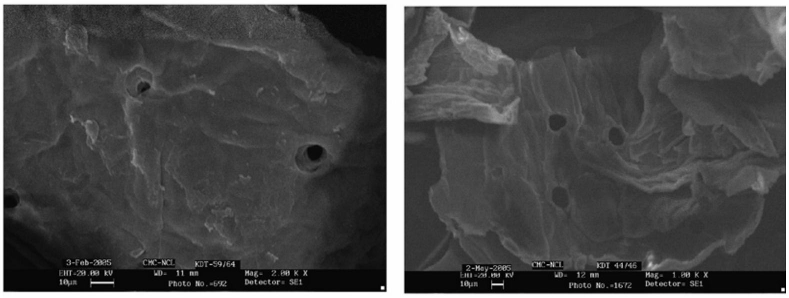
2.3. Scanning electron microscopy studies

The surface morphology of chitosan and various types of crosslinked deacetylated chitin was carried out before and after various types of metal binding by using Leica stereoscan 440 SEM.



Chitosan

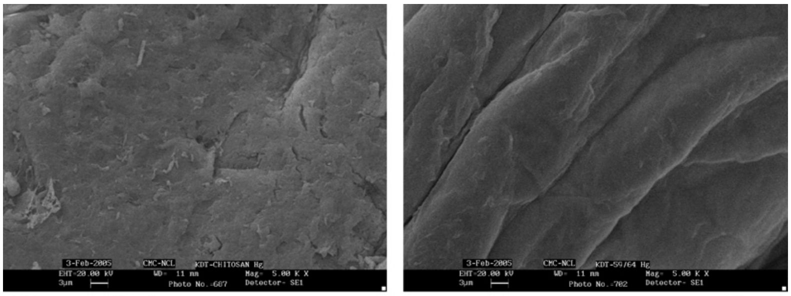
Deacetylated chitin



HDI crosslinked deacetylated chitin

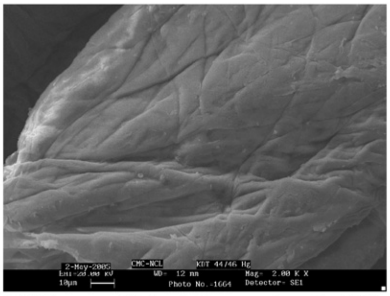
TMA crosslinked deacetylated chitin

Fig. 1. SEM of chitosan, deacetylated chitin and various crosslinked deacetylated chitin.



Chitosan Hg^{++}

HDI-crosslinked deacetylated chitin Hg^{++}



TMA-crosslinked deacetylated chitin Hg^{++}

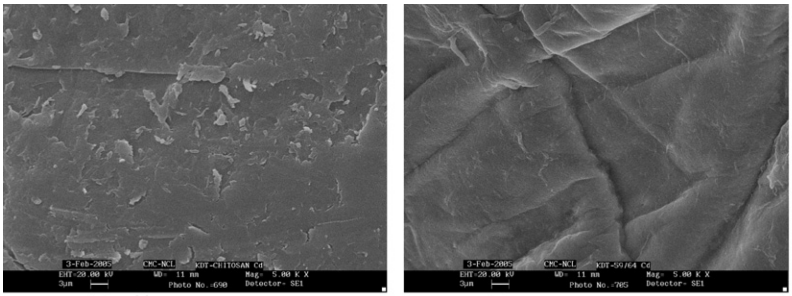
Fig. 2. SEM of Hg^{++} binding on chitosan and various crosslinked deacetylated chitin.

2.4. X-ray diffraction

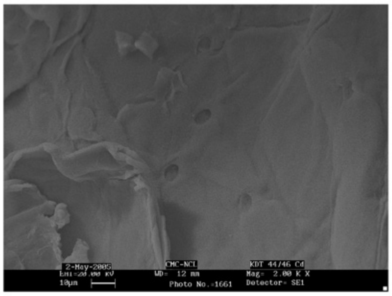
XRD of TMA-crosslinked deacetylated chitin with Cu^{++}, Hg^{++}, Cd^{++}, Pb^{++} metals and without metals were carried out using Philips 1830 XRD.

3. Results and discussion

Fig. 1 shows the surface structure of commercial chitosan (85% deacetylated), deacylated chitin (chitosan) with 88% deacetylation prepared in our laboratory, as well as

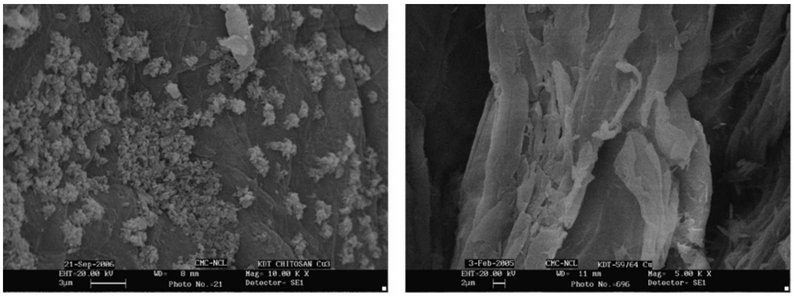


Chitosan Cd^{++} HDI-crosslinked deacetylated chitin Cd^{++}

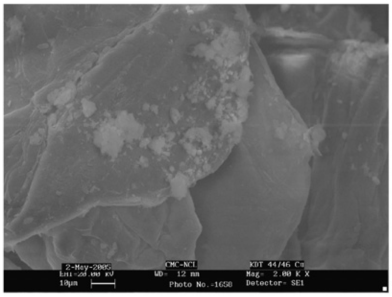


TMA-crosslinked deacetylated chitin Cd^{++}

Fig. 3. SEM of Cd^{++} binding on chitosan and various crosslinked deacetylated chitin.



Chitosan- Cu^{++} HDI-crosslinked deacetylated chitin Cu^{++}

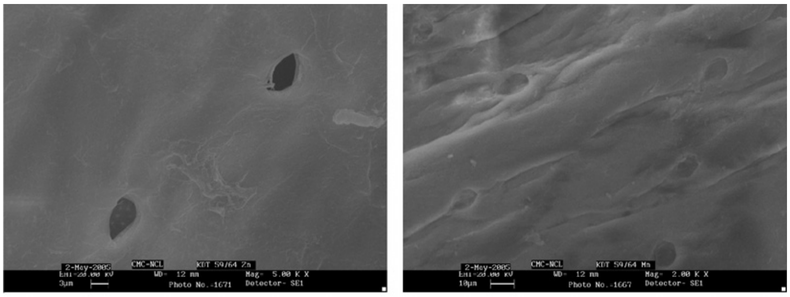


TMA-crosslinked deacetylated chitin Cu^{++}

Fig. 4. SEM of Cu^{++} binding on chitosan and various crosslinked deacetylated chitin.

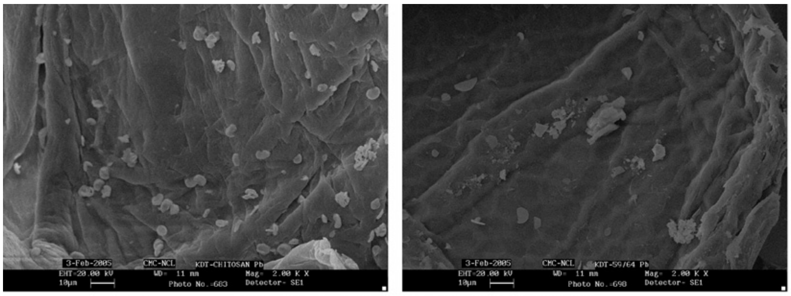
HDI and TMA crosslinked chitosans. The chitosan surfaces are seen to be smooth, but the crosslinked chitosans have large pore structures which are clearly seen. Fig. 2 shows Hg complexed chitosan and crosslinked chitosan. The very strong and specific binding of Hg (372 mg/g chitosan) (Trimukhe & Varma, 2008 and refs. therein) involving most of the amino groups again leads to a smooth surface structure, and the "holes" in the crosslinked chitosan structure (Fig. 1) are not visible due to the significant morphological changes that occur. The same is true for Cu complexes. But Cd, Zn, and Pb which are also strongly bound (133, 92, and 59 mg/g chitosan, respectively) (Trimukhe & Varma, 2008) with the amino groups, but not as strongly as Hg and Cu, shows the presence of some Cd, Zn, and Pb salts on the surface (Figs. 3–5), and the "holes" of the crosslinked chitosan are also still visible. Pb, on the other hand is more weakly bound, and shows more Pb salt on the surface (Fig. 6); here also a few of the "holes" seen in the crosslinked chitosan are visible for the HDI crosslinked chitosan. One would expect Mn, which is very weakly bound to the chitosan (5 mg/g) to also show up on the surface, but the very small amount of Mn present precludes this observation; however, the "holes" seen in the crosslinked chitosan are visible, as they are also for the Zn complexes (Fig. 5).

These morphological studies are well supplemented by our previous morphological studies using WAXRD of chitosan complexed with these same metal ions (Trimukhe & Varma, 2008). Here we clearly showed that the chitosan–Hg complex shows three peaks of crystalline region at 9.76, 21.50, and 28.17°. The main chitosan peak characteristic of chitosan disappears in chitosan–Hg complex due to disruption of the interpolymer bonds. Similarly, the chitosan–Cu complex was characterized by a single broad amorphous peak at 22.16. Thus, complexation of Cu(II) leads to very significant changes in the morphology of the chitosan, indi-

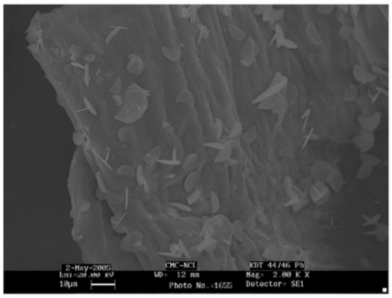


HDI-crosslinked deacetylated Zn^{++} HDI-crosslinked deacetylated Mn^{++}

Fig. 5. SEM of Zn^{++} and Mn^{++} binding on HDI crosslinked deacetylated chitin.



Chitosan Pb^{++} HDI-crosslinked deacetylated chitin Pb^{++}



TMA-crosslinked deacetylated chitin Pb^{++}

Fig. 6. SEM of Pb^{++} binding on chitosan and various crosslinked deacetylated chitin.

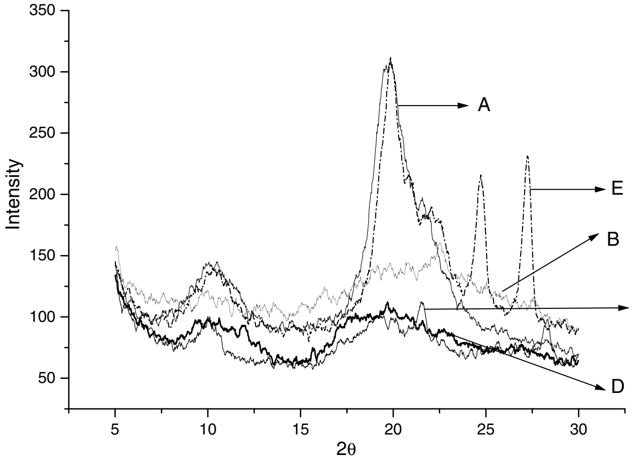


Fig. 7. XRD of (A) TMA-crosslinked deacetylated chitin; (B) TMA-crosslinked deacetylated chitin–Cu complex; (C) TMA-crosslinked deacetylated chitin–Hg complex; (D) TMA-crosslinked deacetylated chitin–Cd complex; (E) TMA-crosslinked deacetylated chitin–Pb complex.

cating complete disruption of the interpolymer bonds. In the case of chitosan–Cd complex we showed 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.

The very small extent of complexation of Pb with chitosan is further proved by the negligible change in the WAXRD spectrum (Trimukhe & Varma, 2008). Exactly the same WAXRD results were obtained with TMA-crosslinked deacetylated chitin, and are shown in Fig. 7 (A–E). The chitosan peaks are seen to disappear with Cu (curve B), Hg (curve C), and Cd (curve D), but not with Pb (curve E) complex.

4. Conclusions

Morphological information gleaned from SEM studies indicate that metal ions like Hg which are very strongly bound to the chitosan and crosslinked chitosans, even to the extent of 360 mg/g, are not seen as distinct moieties on the surface of the polymer, whereas with decreasing extent of binding, in the order Hg > Cu > Cd > Zn > Pb > Mn, we begin to observe the increasing presence of metal on the surface. These results agreed with the morphological information obtained with WAXRD studies, as well as with the metal complexation data of these metals with these same chitosan polymer/crosslinked polymer systems.

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