

Spectroscopic Studies on Biodegradable Polymer Blend Having Antimicrobial Biological and Adsorbent Property used in Wastewater Treatment[†]

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Abstract: Clean drinking water paves way to a healthy human race. The key solution to this problem is to develop an efficient and cost effective purifying technology using natural and modified adsorbents. Chitosan, a biodegradable polymer can be used as a stand alone membrane. Chitosan and nylon 6-synthetic polymer blend and chitosan and clay-natural polymer blend, have been attempted in the present study to regenerate water from industrial wastewater effluent. As adsorbent for the removal of heavy metals from water, biopolymers have been studied. In the present study, chitosan was blended with clay membrane and was used in removing copper and cadmium from synthetic industrial wastewater. Attention was focused on the spectroscopic properties of chitosan-nylon 6, chitosan-clay membranes and were compared. This is to understand the various interactions of the groups in clay, which are not present in nylon 6. The polymer blends were synthesized and characterized using FT-IR, XRD and TGA/DTA. The results showed that the polymer blends possess antibacterial property in addition to being good adsorbents. Results are presented and discussed.

Keywords: Chitosan, Clay, Nylon 6, Antimicrobial activity

Introduction

Clean drinking water is the main issue to have a healthy human population. By extensive use of chemicals and due to rapid industrialization, water gets polluted. Problems in drinking water quality include the presence of excess fluoride, arsenic and natural organic matters, heavy metals and a variety of pathogens. Cost effective and efficient use of natural and modified adsorbents is the solution to this problem. Several natural adsorbents are being used for the treatment of contaminated drinking water and its sources. Chitosan which is a biodegradable polymer can be used as stand alone membrane or chitosan and nylon 6, which

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are synthetic polymer blend and chitosan and clay which are a natural polymer blend, have been attempted in the present study to regenerate water from wastewater effluent from the industries. Clay minerals are widely used because of their high specific surface area, chemical and mechanical stability, a variety of surface and structural properties and low cost¹⁻⁴. Ion exchange methods like reverse osmosis process is usually followed not only in removing heavy metal ions but also for purification of water. Generally adsorption is the main underlying principle in these processes. Biosorption technique involves active and non active uptake by biomass and is a good alternative to the traditional processes. These processes seem to be not only eco friendly but also recyclable and hence attempts have been made in this work to synthesize bio degradable polymers which will be used to remove heavy metals. In the case of bio-polymers chitin, chitosan, clay and nylon 6 and glutaraldehyde are widely employed as bio polymers. Biopolymers have been studied as adsorbents for the removal of heavy metals from water. Chitosan is the one of them^{5,6}. It has a better adsorption capacity for metal ions. It has severe limitations in its use in acidic media because of its solubility in acid^{7,8}. In the present study chitosan is blended with clay membrane and is used in removing copper and cadmium from synthetic industrial wastewater.

Experimental

Chitosan (90%) from DNP International (city and state) was used to make all chitosan solutions. Chitosan solutions from 2 to 20 g/L were used for the experiments. The powdered chitosan was weighed and dissolved in 0.05 M or 0.01 M acetic acid depending on the pH required. Slight adjustments in pH were made using 1 M acetic acid. Standard heavy metal stock solutions (1000 mg/L) was prepared by dissolving 200 mg/L CuCl₂, 200 mg/L CdCl₂. pH adjustment of solutions were made using dilute or concentrated NaOH (Sigma Chemicals Co.) and HCl (Sigma Chemicals Co.) solutions using Orion 420 A pH meter. All the reagents were of analytical grade and stored in polyethylene polypropylene containers.

Preparation of nylon 6

Nylon 6 in pellet form was obtained from DuPont and had a molecular weight of 19,000. Chitosan (92% deacetylated) was obtained from India Sea Foods, Cochin.

Preparation of clay

The suspension of kaolin clay was prepared by mixing 1 g of clay in 25 mL of de-ionized water and stirring in moderate speed for 20 min.

Anti microbial activity

The assay was carried out by well diffusion method. Muller Hinton Agar plates (Bacteria) and Potato Dextrose Agar (Fungi) were spread with respective culture using a swab and wells are bored in each plate at the diameter of 6 mm each. The wells were filled with polymer blends [(chitosan/nylon 6(1:1); chitosan/clay (1:1)] at the of concentration of (25 µg/well respectively). The bacterial plates were incubated at 37 °C for 24 h and the plates holding fungal cultures were incubated at 28 °C for 72 h. The zone of inhibition (ZOI) was measured by subtracting the well diameter from the total inhibition zone diameter. *Chloramphenicol* (30 µg/disc) and *Amphotericin B* (100 unit/well) used as positive control for bacterial and fungal species, the assays were performed in triplicate.

Results and Discussion

FTIR spectra analysis

Figure 1 compares the FT-IR spectrum of chitosan and chitosan and nylon 6 (1:1). As per⁹ the peak at 1628 cm^{-1} has been assigned to water. But the peak at 1087 cm^{-1} may be due to C-O-C stretching in the spectrum of pure chitosan. According to¹⁰ the amide group band of chitosan will appear at 1628 to 1650 cm^{-1} . The shift of the bands in these areas is attributed to the molecular miscibility of the polymers. On the contrary inter hydrogen bonds are formed between chitosan and nylon 6. For pure chitosan and nylon 6 the displacement number was about 25 cm^{-1} (from 1650 to 1628 cm^{-1}). This may be due to the chelation effect caused by the coordination interaction between NH_2 groups of the chitosan and nylon 6¹¹.

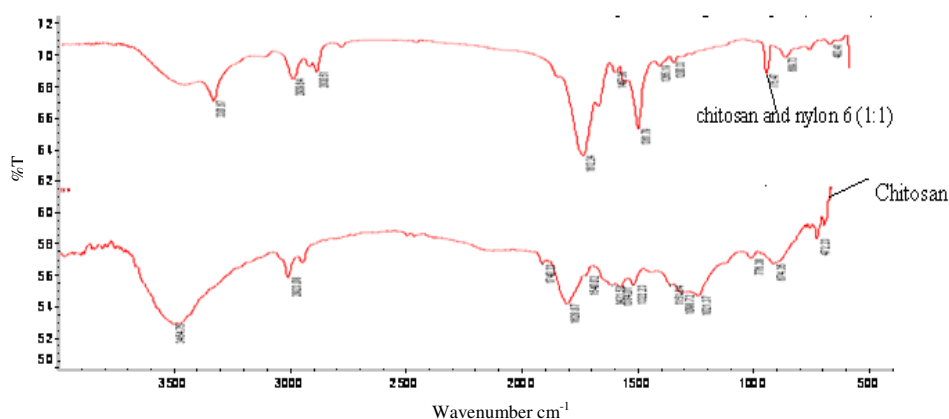


Figure 1. FT-IR spectrum of chitosan, nylon 6 (1:1)

Figure 2 shows the FT-IR spectrum of chitosan and clay. The main vibration bands in this spectrum are at 3622 cm^{-1} (for O-H stretching) at 3428 cm^{-1} (due to interlay red O-H stretching) H- bonding at 1635 cm^{-1} (for H-O-H bending) 957 cm^{-1} and 845 cm^{-1} (for Si-O stretching) at 542 cm^{-1} (for Si-OH stretching peaks¹² and 520 cm^{-1} and 430 cm^{-1} . The peaks of $-\text{NH}_2$ groups in pure chitosan at 1643 and 1578 cm^{-1} are shifted to 1635 cm^{-1} in the chitosan and clay, corresponding to the deformation vibration of amine group of chitosan¹³.

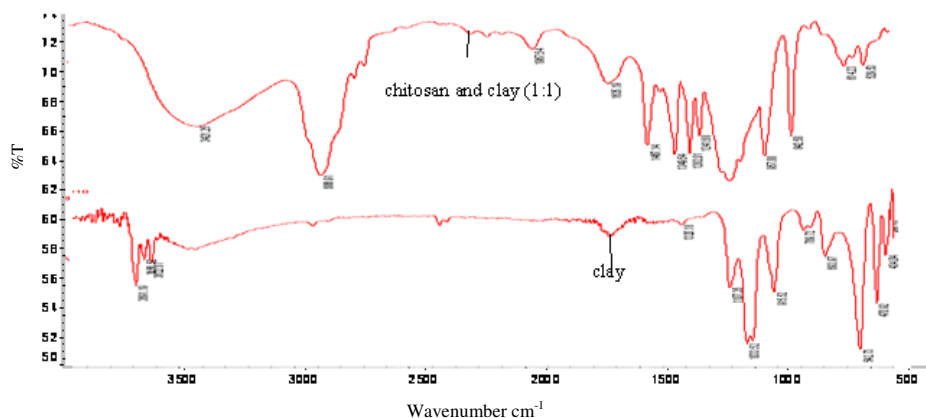


Figure 2. FT-IR spectrum of chitosan, clay (1:1)

The peak at 915 cm^{-1} may be due to Si-O stretching and the peak at 542 and 470 cm^{-1} may be due to Si-O bending. The peak at 3622 cm^{-1} is missing in this figure and the O-H stretching would not have been there since this would have been due to complexation of clay with chitosan. At 1635 cm^{-1} there is a peak which may be due to H-O-H bending. This may also be due to the overlapping of H-O-H bending peak with N-H bending peak. This might have resulted as a deformation vibration peak of amine of chitosan. The peak at 1633 cm^{-1} is due to H-O-H bending vibrations. This may also be due to deformation peak of amine of chitosan with clay. Disappearance of peaks at 1368 cm^{-1} and 1308 cm^{-1} for clay and chitosan and existence of peak at 1382 cm^{-1} may be due to complexation between the amino groups of chitosan and clay. The peak at 1628 cm^{-1} indicates the complexation between the amino groups of chitosan and clay. As already discussed this peak may also be due to deformation and vibration of amine of chitosan.

X-Ray diffraction analysis (XRD)

Figure 3 shows the XRD data of pure nylon 6. As it is, it gives the information that the state is amorphous and there is sharpness at two places. They are at 19.690 and 440 . A pure chitosan film shows four main diffraction peaks These confirm the presence of more polymer domains in its structure. This is in good agreement with the results reported by¹⁴. The diffractograms of pure chitosan and blend indicate that the materials are amorphous. From the diffractograms of pure chitosan and blend with nylon 6 (1:1) of chitosan indicate the presence of chitosan in general and miscibility of the polymer with blended polymer in particular. In general, the diffractogram containing 1:1, is similar to pure chitosan and this suggests that the polymers are miscible. This is understandable from the fact that the presence of hydrogen bonding via residual water molecules forms the blend and this is in agreement with¹⁵. In this residual water, the molecules will act as an active compatibilizer in the blend.

IR spectroscopy may be an appropriate technique to study the biopolymer clay interaction, since a shift in the NH_3 vibration has been reported when chelating transition metal ions by chitosan takes place. A similar behavior may also be expected when $-\text{NH}_3 +$ groups interact electrostatically with the negatively charged sites of the clay. In fact, a shift of the NH_3 band towards a lower frequency is observed in all the chitosan montmorillonite nanocomposites Figure 3. Besides, the intensity of the NH_3 band also increases for higher amounts of chitosan. The amide I band at 1650 cm^{-1} of chitosan is overlapped with the H-O-H bending vibration band at 1640 cm^{-1} of the water molecules associated to the nanocomposites, which are present in a similar amount than in the starting clay, as expected for a biopolymer with high water retention capability.

Thermo gravimetric analysis (TGA)

The second thermal event for pure chitosan and blend with nylon 6 is observed at about $300\text{ }^{\circ}\text{C}$ with the maximal rate at $355\text{--}356\text{ }^{\circ}\text{C}$ and is related to degradation, which includes the parallel processes of dehydration and demethoxylation. The degradation profile of chitosan is in good agreement with similar results reports¹⁶. The degradation profile of the blends containing 1:1 consists of the events typical for both chitosan and nylon 6. This behavior could be observed for degradation of mechanical mixtures of the polymers and indicate on their miscibility in the blend. However, the degradation of the blend containing of chitosan shows only events characteristic for pure cellulose ether. The absence of the event typical for pure chitosan at $250\text{--}350\text{ }^{\circ}\text{C}$ in this blend indicates on some interactions between the polymers and may be considered as a proof of their partial miscibility.

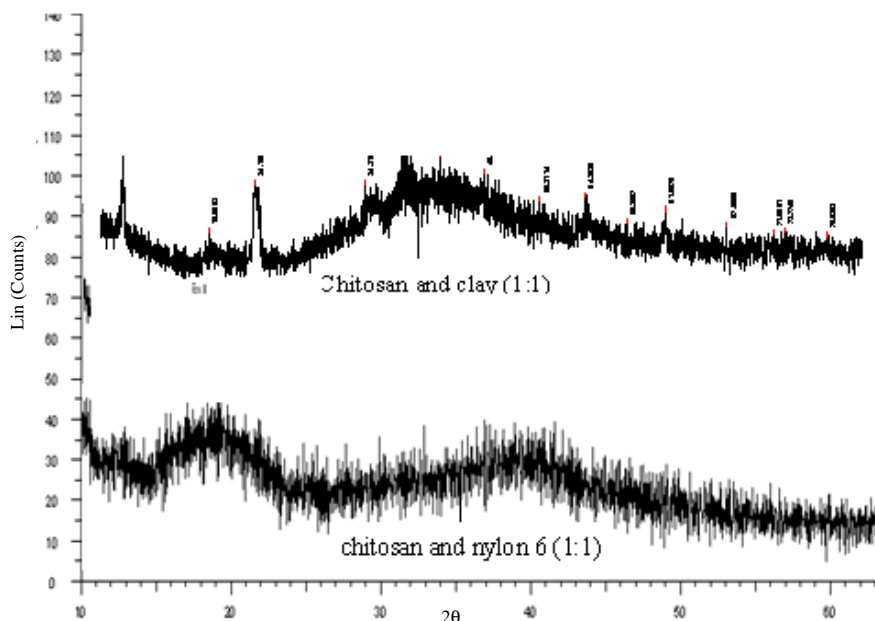


Figure 3. XRD pattern of chitosan, nylon 6 and clay (1:1)

Thermogravimetric data of chitosan with clay particles are shown in Figure 4. All chitosan films were degraded at 286–297 °C. This agrees very well with the results reported by^{17,10}. The increase in the degradation temperature is generally regarded as a consequence of the low permeability of the clay like materials preventing oxygen to reach the polymer, and preventing the volatiles generated during the decomposition of the polymer to leave the clay.

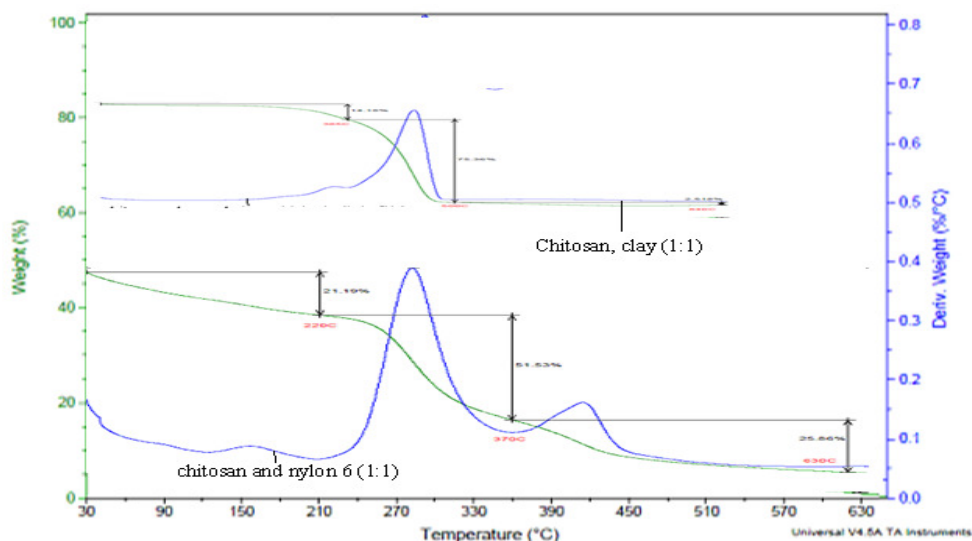


Figure 4. TG/DTG of chitosan, clay, nylon 6 (1:1)

Differential scanning calorimetry (DSC)

Figure 5 shows the thermal properties of the chitosan, nylon 6 blended membranes. Glass transition temperatures (T_g) were not observed both for chitosan and nylon 6. A broad endothermic was observed around 60 °C for the chitosan, nylon 6 membrane, which is an endothermic peak that exists for most polysaccharides at low moisture contents¹⁰. In the nylon 6 curve, a melting endothermic peak was observed at 225 °C, which was associated with the crystalline polymer fraction. The characteristic peak of chitosan at about 60 °C became smaller with increasing nylon 6 content and the melting peak of nylon 6 at 230 °C became smaller with decreasing the nylon 6 content, but no obvious change in the melting temperature was observed¹⁸. This indicated that the nylon 6 crystallization decreased after blending with chitosan, and there was interaction between chitosan and nylon 6.

From Figure 5, it is seen that differential scanning calorimetric data can be obtained for (1:1), however no meaningful DSC data could be obtained. This may be due to melting or thermal event that could have been delayed unlike in the other two cases. The first endothermic peak that occurs in the temperature range of 265.13 °C may be attributed to solvent evaporation¹⁰. The peak in the range of 230 to 520 °C indicates crystallization of the chitosan. This process is not inhibited by clay particles, this is evident from the appearance of the peak and there is no shift in the peak position as the content of clay is increased.

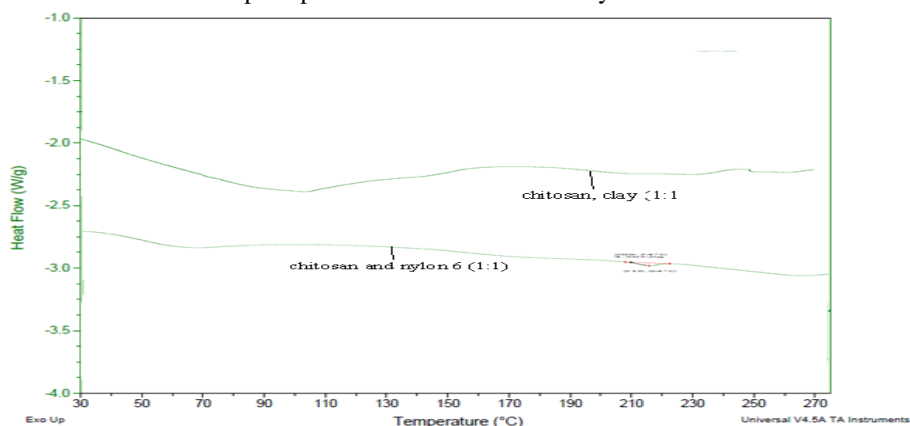


Figure 5. DSC of Chitosan, clay, nylon 6 (1:1)

Antimicrobial activities

Figure 6 and Figure 7 show antimicrobial activity of chitosan and nylon 6 and chitosan and clay. Chitosan has been studied in terms of bacteriostatic/bactericidal activity to control the growth of *chloramphenicol* and to inhibit viral multiplication¹⁹. Moreover, towards mammalian cells chitosan, nylon 6 and clay possess antimicrobial activity. This is because they have higher killing rate and lower toxicity towards these cells. The blend with low content of chitosan has less antibacterial effect for all bacteria under test. At the same time, the antimicrobial activity of the blended composition increases with increasing the content of chitosan in the polymer blends. This phenomenon may be related to the presence of a lot amount of net positively charge in the chitosan macromolecules. But this is less pronounced in the case of blend with synthetic polymer *viz.*, nylon 6 where there is less porous nature²⁰. The same is more pronounced in the case of blend with natural polymer, *viz.*, clay where there is more porous compared to nylon 6.

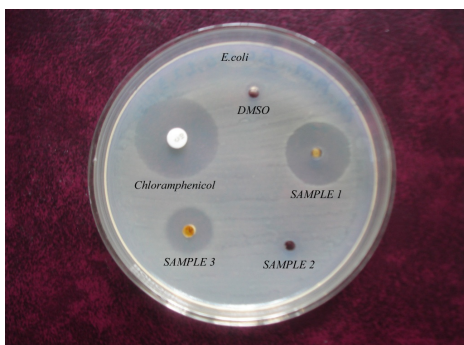


Figure 6. Antibacterial activity of chitosan/nylon 6 (1:1)

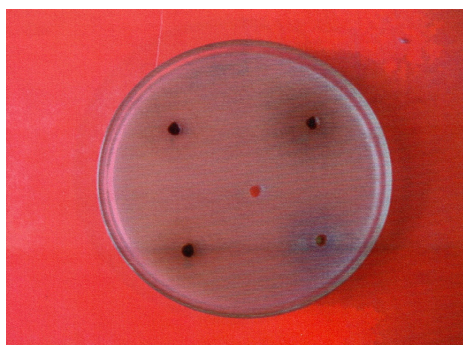


Figure 7. Antibacterial activity of chitosan/clay (1:1)

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