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Selective adsorption properties of chitosan membranes

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ABSTRACT

Chitosan is a natural carbohydrate biopolymer derived by deacetylation (DA) of chitin, a major component of the shells of crustacea such as crab, shrimp, and crawfish. Like cellulose, chitosan is a fiber. However, unlike plant fiber, chitosan possesses unique properties that may be enhanced by forming it in thin film or membrane structure. The chitosan films have enormous surface area per unit volume (high aspect ratio), which provide remarkable capacity for attachment or release of functional groups, absorbed molecules, ions and particles of many kinds. This work deals with formation of chitosan membranes (films) to study the selective adsorption property of heavy metal ions present in leather tanning effluents. Chitosan was prepared from the chitin by deacetylation process. The degree of deacetylation was determined and molecular weight was calculated. The chitin and chitosan were characterized with FTIR. The synthesized chitosan was fabricated into membranes, whose surfaces were analyzed with scanning electron microscopy (SEM) and optical spectroscopy. The SEM images show the porous nature of the membrane indicates the possibility of metal ion adsorption. The complete absorption spectra of chitosan membranes show the absorption peak around 330nm specify the selective adsorption nature of the carcinogenic and dangerous species of the effluent (Cr-VI) by the chitosan membranes. Heavy metal adsorption property of the chitosan depends on time of adsorption, thickness and area of the membrane. The linear variation of absorbance with time indicates the fast absorption rate of the metal ion by the chitosan membranes. The mechanism of the selective adsorption is due to physic-sorption process.

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Introduction

Rapid industrialization, large scale urbanization involves the use of chemicals containing toxic elements and heavy metal ions that resulted in the increased contamination of our environment. Metallic pollution specifically caused potential danger to the mankind as the heavy metal ions are dumped into the surroundings in the form of industrial effluents. A lot of research has been carried out to alleviate or at least minimize the effect of the heavy metal ions from industrial waste waters in environmental pollution. Several ways and means including filtration, chemical precipitation, ion exchange, adsorption, electro deposition and the use of membrane systems have been developed [1-8]. Each of the above methods has its own advantages and disadvantages. Any method chosen for that matter need to be environment friendly as the method itself should not be counter- productive to the surroundings.

Adsorption method is found to be relatively convenient and economical in addition to catering to our prime objective of not to affect the environment. In recent years, studies on biopolymers, which adsorb metal ions, have increased substantially that attract greater interest in terms of their efficiency, wider availability and environmental safety. Biopolymers like Chitin and chitin derivatives have been applied successfully for the removal of traces of heavy metals, dyes and radioactive waste. The effectiveness of chitosan to remove lead and cadmium in drinking water has been demonstrated by Knorr [9]. Chitosan from treated crab shells have also been used effectively to treat effluents from electroplating industry and for the removal of hexavalent chromium [10, 11]. Therefore, studies on the interaction of ions with chitin and chitosan are of importance in ecology not only in connection with water pollution but also with ionic equilibria in uncontaminated natural waters [12].

A systematic analysis of literatures reveals that studies on heavy metal absorption by chitin and chitosan are plenty. However the cost involved in this process is heavy, since it requires materials in bulk form. At the same time for certain specific applications, chitin and chitosan in bulk form is unsuitable [13]. Therefore, preparing this material in thin film form is valuable and improves its physical and chemical character. It is very difficult to dissolve chitin to make it as thin films. Therefore chitosan is selected as a suitable candidate, which can be easily dissolved in organic solvents and can be made as free standing film, which can act as membrane for metal absorption. The objective of the present work is to synthesis chitosan from chitin and measure the degree of deacetylation using FTIR measurements. The chitosan membranes thus prepared were subjected to selective absorption property of chromium ions present in the leather effluents.

Experimental

Synthesis of chitosan

About 10g of pure chitin was hydrolysed by heating to 100°C with 50% NaOH solution under reflux for 2 h by the method [14]. This yielded 50%-75% deacetylated chitin (chitosan). The deacetylated chitin is then washed with distilled

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water to remove excess NaOH, rinsed with methanol and then with acetone. Then dried in oven and stored in airtight container.

Preparation of chitosan membrane

Chitosan solutions were prepared by mixing 0.1 g of finely grinded chitosan powder with 5 ml of acetic acid in a 100 ml glass beaker. This solution was stirred for about 1 hour continuously using a Teflon pellet, which was rotated with a help of a magnetic stirrer maintained at room temperature to form a 2 wt % solution. Most of the chitosan dissolved to give a transparent solution. Minor insoluble solids were removed using a What man 4 filter paper. This solution was cast into films using a 17.8×17.8 cm glass mold. After solvent evaporation, the films were soaked in 1 N NaOH for 1h to remove residue acid. The films were then washed with a large quantity of distilled water several times until the wash was neutral followed by drying first on a piece of glass with film's edge clamped and finally, in a oven (50ºC, 24h). The resulting films were 25±0.1 µm thick.

Characterization

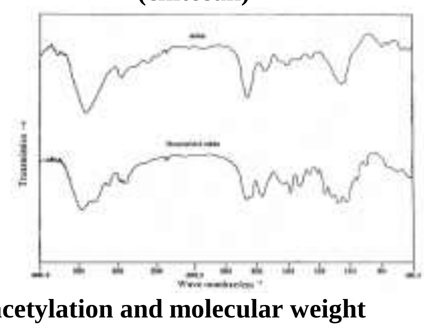
Transmittance spectra were used to quantify the characteristic peaks of the synthesized chitin and chitosan powder in the wavelength range of 400 – 2000 cm^{-1} using a Bruker IFS - 66V spectrometer. Optical absorptions were recorded on UV-Visible double beam Spectrophotometer (Thermo Vision) in the wavelength range of 200 – 900 nm with the spectral resolution of 1nm. The morphology of solution cast chitosan films were investigated using JSM 35 CF JOEL model scanning electron microscopy (SEM) with a resolution of about 30 to 150 Å.

Result and Discussion

Infrared analysis

The chemical property of chitosan can be identified from IR spectrum. It has three main absorption bands have been detected in chitosan samples (Fig.1) namely: the band in the range 3500 ± 2500 cm^{-1} corresponding to the vibrations of OH, NH and CH groups, the complex band in the range 1690 ± 1300 cm^{-1} corresponding to absorption of carbonyl and amide groups (Amide I band at 1655 cm^{-1} and Amide II band at 1550 cm^{-1}), the strong absorption band between 800 and 1200 cm^{-1}, which is characteristic of pyranose rings of chitosan matches with the reported result [15].

Fig. 1. FTIR spectrum of chitin and deacetylated chitin (chitosan)



Degree of deacetylation and molecular weight

Physical properties of chitosan are governed, at large, by two factors; the degree of deacetylation (DD) and the molecular weight. Degree of deacetylation has a direct [16] impact on the secondary structure of the polymeric chain and can also influence the solubility of the polymer in organic or aqueous solvents. The degree of deacetylation (DD) value of chitin was calculated from FTIR analysis from the following formula.

$$DD\ (\%) = [1-(A_{1655} / A_{3450}) \times 1/1.33] \times 100$$

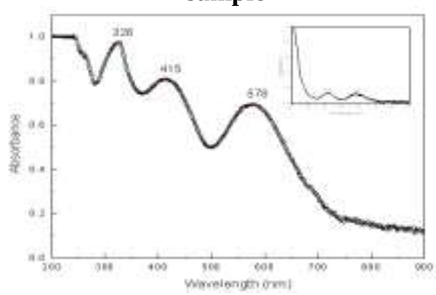
where A_{1655} – Absorbance value at 1655cm^{-1} for carbonyl peaks and A_{3450} – Absorbance value at 3450 cm^{-1} for hydroxyl peaks. The optimized value of the degree of deacetylation and found to be 40- 75%, which is sufficient for the complete dissolving of the prepared chitosan sample in acetic acid.

Intrinsic viscosity is an important parameter in polymer characterization and is of particular value in the estimation of average molecular weight. There are many equations used to find the intrinsic viscosity of variety of polymer solvent systems when the single relative measurement is made at low concentration. The values of the viscosity and intrinsic viscosity were measured for chitosan + acetic acid system and calculations had been carried out to measure the molecular weight, found to be around 4000 g/mol.

Optical absorption analysis and scanning electron microscopy

The problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems. Toxic metal compounds coming to the earth's surface not only reach the earth's water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow. Therefore, the earth's waters may contain various toxic metals. Leather industrial effluent mainly contains chromium III (Cr-III), chromium VI (Cr-VI), proteins and some minerals. Out of these various components Cr-VI is the carcinogenic species that cause cancer in living beings. In order to study the selective adsorption property, the chitosan membranes were immersed in the effluent samples for different time intervals (0, 30, 60, 90 and120 minutes) collected in a leather industry (NMZ Tanners - Ambur). The optical absorption properties of the effluent (Fig.2) samples show peaks at 326, 415 and 578nm.

Fig.2 shows the typical absorbance peaks of the effluent sample



The peak at 326nm is due to chromium –VI species that was well documented in several literatures [17-19]. The peaks 415 and 578nm are due to chromium –III species which was verified with the help of standard chromium solution (Fig 2 inset). The complete absorption spectra of chitosan membrane show the absorption peak around 330nm as shown in Figure 3. This indicates that the chitosan membranes selectively adsorbed the dangerous species of the chromium (Cr-VI) in the effluent.

Fig.3 Optical absorbance spectra of chitosan films

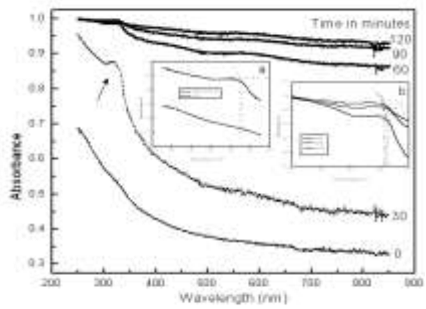
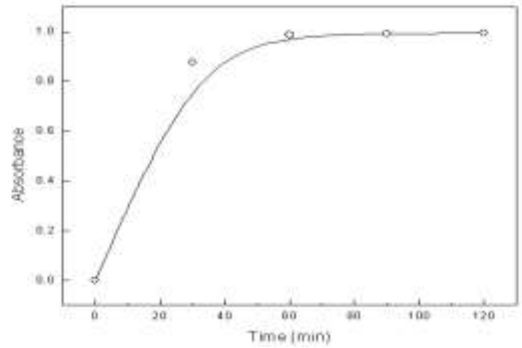


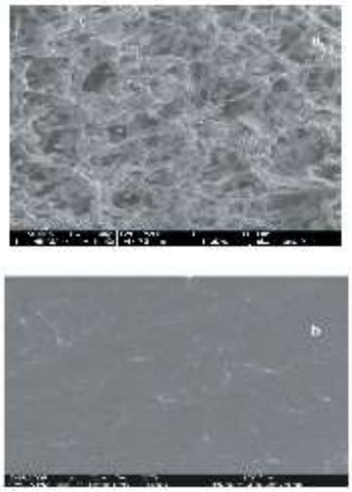
Fig 3 inset (a) and (b) shows the selective part of the graph drawn to the correct peak positions. Since the instrument used is having an accuracy of ± 1nm, the error in the measurement of the peak positions are with in the limits. The adsorption of Cr-VI starts immediately after the immersion of the chitosan films in the effluents. The adsorption gets saturated around two hours. The maximum adsorption found within 30 minutes as shown in Figure 4.

Fig.4 shows the variation maximum absorbance with time



The adsorption mechanism of chitosan can be explained as follows. Chitosan have different functional groups, such as hydroxyls and amines (anions) to which the chromium metal ions (cations) can bind either by chemisorptions or by physic-sorption process. The SEM image shows porous nature of the chitosan membrane (Fig 5a) which is the pre-requisite for membrane filtration. Fig 5b shows Cr-VI adsorbed chitosan membrane surface.

Fig. 5 (a) SEM image of chitosan membrane; (b) SEM image of Cr-VI adsorbed chitosan membrane



Conclusion

The Chitosan fabricated in membrane form provide enormous surface area per unit volume which enhances the capacity for attachment of the chromium metal ion on its surface. A stack of chitosan membranes arranged in an effluent unit may facilitate the online removal of carcinogenic chromium species. Further studies on various parameters of heavy metal adsorption in chitosan membrane both qualitatively and quantitatively will through more light on this material.

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