UGC Minor Research Project Report

Project Title: “Preparation of Chitosan based composite membranes for sorption of heavy metals from aqueous samples.

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Amount Sanctioned: Rs 90,000/-

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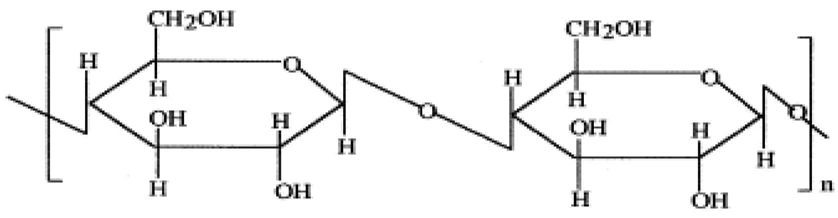
1. Introduction

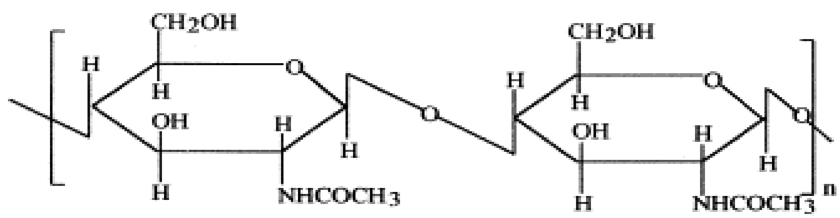
Industrial waste water released from paint industry, dyes and metal industries is a major source of chromium. Out of the two stable oxidation states of chromium Cr^{6+} is more mobile and toxic. Cr^{6+} is easily absorbed by human cells and is reduced to pentavalent chromium and finally to Cr^{3+} by vitamin C during which it causes breakage in the DNA and hence is highly genotoxic which leads to various types of cancers. Removal of chromium from water is of major concern as far as environmental serenity is concerned. There are various methods which are available for removal of this metal from aqueous samples. However most of the methods of removal are expensive and require complex procedures. Adsorption of chromium by using synthetic polymers is one of the promising methods. The major problem associated with synthetic polymers is that they are not biocompatible and biodegradable. One of the biodegradable and biocompatible polymers abundantly available in nature is chitin.

Chitin is the second most abundant polysaccharide after cellulose on the earth. It is composed of β (1→4) linked 2-acetoamido-2-deoxy-β-D glucose.

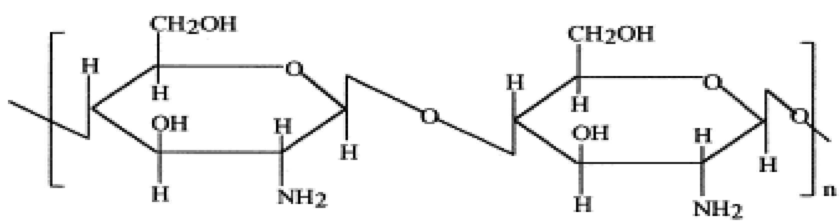
It is a white hard elastic nitrogenous polysaccharide found in the exoskeleton as well as internal structure of crustaceans like prawns lobsters etc. Chitosan is the N-deacylated product of chitin.



Cellulose



Chitin



Chitosan

Chitosan is soluble in dilute acids like acetic acid and has unique physical and mechanical properties. It has a reactive hydroxyl and amino group due to which it forms complexes with many transitional metal ions. Chitosan shows unique combination of properties like biodegradability, biocompatibility and bioactivity in addition to excellent physical and mechanical properties. Due to these excellent properties chitosan is an attractive reagent for removal of metallic impurities in industrial waste water.

Chitosan shows good complexation with metal ions in acidic medium due to the protonation of NH_2 group to form NH_3^+. However due to more solubility of chitosan in acidic solutions this property is difficult to achieve at low values of pH. To decrease the solubility of chitosan in acidic solutions and to increase its mechanical strength crosslinking between the chains of chitosan can be done by the use of crosslinkers. In literature crosslinking of chitosan has been reported by the use of crosslinkers like Ethylene diamine tetra acetic acid (EDTA), Epichlorhydrin and gluatraldehyde. Chitosan has been employed in the powder form and has also been casted into films for the uptake of metal ions. These films have been used in the natural as well as crosslinked form for the uptake of various metal cations like Cu^{2+}, Cd^{2+}, Cr^{6+} ,Pb^{2+} etc from aqueous samples. However these films are not selective towards the uptake of a particular metal ion.

2. Objectives

- The main objective of the study was to prepare chitosan composite membranes using specific dyes and crosslinkers for the sorption of heavy metals like chromium, cadmium and mercury from aqueous samples.
- Optimization of parameters like the percentage of chitosan, degree of acetylation in the chitosan, use of crosslinking reagents, derivatization using specific reagents, optimum membrane thickness for the preparation of membranes were to be optimized.
- Sorption of heavy metals in the optimized membranes

3. Experimental

a. Preparation of natural chitosan films

Chitosan was dissolved in acetic acid solution. The solution was ultrasonicated for 3-4 hours for better dissolution. The solution was then poured into petriplates having inner diameter of about 8 cm. The petriplates were then kept in an oven at 60 ^{o}C till evaporation of the solvent took place and thin films were formed. The films were then thoroughly washed with distilled water to dried at room temperature. The films were then cut into 1 cm × 2 cm pieces and stored in water. About 14, 1 cm × 2 cm pieces were obtained from one film.

b. Crosslinking of natural chitosan films

The natural films were then crosslinked using gluatraldehyde solution for 4 h followed by washing with distilled water. The films were then washed with water, excess water was removed and stored in air tight containers till further use.

c. Treatment of natural and crosslinked chitosan films with 1,5 Diphenyl carbazide

The pieces of natural and crosslinked chitosan films were then soaked in a solution of 1,5 diphenyl carbazide . The films were then removed, washed with distilled water and stored for further use.

d.Sorption of Cr^{+6} in natural, crosslinked and DPC treated films

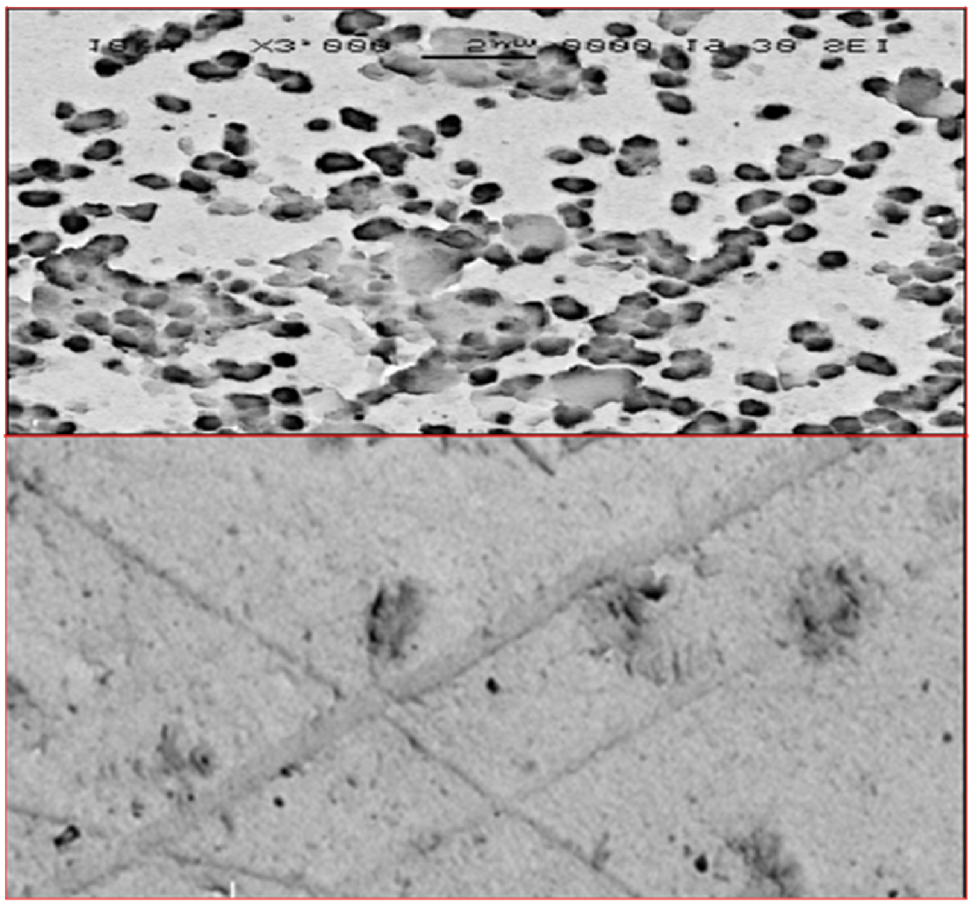
A stock solution of Cr^{6+} having a concentration of 1000 ppm was prepared using A.R grade potassium dichromate. The pH of this solution was adjusted to the required pH in the range of 2 to 9 using NaOH or H_2SO_4 solution (0.1 M). This solution was then diluted to obtain standard solution in the concentration range of 10 to 100 ppm. 50 mL solutions of these diluted solutions were allowed to equilibrate with 1 × 2 cm^2 pieces of all the three types of films i.e. natural chitosan film, crosslinked chitosan film and crosslinked films treated with DPC. The concentration of Cr^{6+} in the solutions used was measured both before and after equilibration with the films. Cr^{6+} concentrations were measured by using spectrophotometric method by reaction with diphenyl carbazide in acidic medium.

Cr^{6+} concentrations in the residual solutions were measured at intervals of 24 hr till constant readings were obtained.

e. Charcaterization of the films: Characterization of the films was done using TGA and Scanning electron microscopy.

Following figure shows the SEM images of natural and crosslinked films

Natural chitosan and Crosslinked chitosan SEM images



4. Results and Discussion:

In the present work we have prepared gluatraldehyde crosslinked chitosan films for the uptake of Cr^{6+} ion. The crosslinked films have been treated with a solution of Diphenyl Carbazide (DPC) which is highly specific for Cr^{6+} ion. The uptake of Cr^{6+} ion in natural chitosan films, crosslinked chitosan films and DPC treated films has been studied spectrophotometrically. The effect of various experimental conditions like chromium ion concentration, pH, time of equilibration were studied and evaluated. The changes in the structure of the films due to crosslinking and treatment with DPC were studied using Thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM). The DPC treated films showed higher uptake of Cr^{6+} over the natural chitosan and crosslinked chitosan films.

Comparison of extraction efficiency of natural, crosslinked chitosan and DPC treated membranes. Following table gives a comparison of the extraction efficiencies of the prepared films.

Type of material	**Initial Cr^{+6} ppm**	**Extraction in 24 h**	**Extraction in 48 h**	**Extraction in 72 h**	**Extraction in 96 h**
Natural Chitosan membrane	**50 ppm**	**1.7%**	**6.5%**	**12.5%**	**15.5%**
Crosslinked Chitosan membrane	**50 ppm**	5.0%	25.4%	50.9%	65.4%
Crosslinked membrane + DPC	**50 ppm**	67.8%	82.8%	91.4%	92.4%

5. Outcome of the work: The proposed work has resulted into Cr^{6+} selective natural and crosslinked chitosan films which have been optimized for the removal of Cr^{6+} from simulated effluent water samples

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