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Comparative studies on the removal of heavy metals ions onto cross linked chitosan-g-acrylonitrile copolymer

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ABSTRACT

The graft copolymerization of acrylonitrile onto cross linked chitosan was carried out using ceric ammonium nitrate as an initiator. The prepared cross linked chitosan-*g*-acrylonitrile copolymer was characterized using FT-IR and XRD studies. The adsorption behavior of chromium(VI), copper(II) and nickel(II) ions from aqueous solution onto cross linked chitosan graft acrylonitrile copolymer was investigated through batch method. The efficiency of the adsorbent was identified from the varying the contact time, adsorbent dose and pH. The results evident that the adsorption of metal ions increases with the increase of shaking time and metal ion concentration. An optimum pH was found to be 5.0 for both Cr(VI) and Cu(II), whereas the optimum pH is 5.5 for the adsorption of Ni(II) onto cross linked chitosan-g-acrylonitrile copolymer. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. Adsorption isothermal data could be well interpreted by the Freundlich model. The kinetic experimental data properly correlated with the second-order kinetic model. From the above results it was concluded that the cross linked chitosan graft acrylonitrile copolymer was found to be the efficient adsorbent for removing the heavy metals under optimum conditions.

1. Introduction

The continuous increase of water pollution was mainly due to the progressive increase of industrial technology. For minimizing these hazardous pollutants a great effort has been done. The effort was mainly taken to avoid the dangerous effects caused by the pollutants on animals, plants and humans. Contamination by the heavy metal has become a main critical problem recently because the metals gets persisted and accumulated in the environment [1,2]. The toxic metal compounds contaminate underground water in trace amounts by leaking from the soil after rain and snow [3]. The effluents of industrial wastewaters often contain considerable amounts of toxic and polluting heavy metals such as chromium, mercury, lead, copper, etc [4].

Toxic metals ions in trace quantities are difficult to remove from aqueous solution. Adsorption is the promising alternatives for removing the toxic metal ions in trace quantities from aqueous solutions especially using low-cost adsorbents like clay material, agricultural wastes and seafood processing wastes [5]. The new technology searches have directed attention to biosorption for removing the metal ions from waste water, based on metal binding capacities of various biological materials. Recently there is an increasing interest in the application of materials having biological origin in the removal of heavy metal ions from aqueous solutions.

Since the cost of these materials is much lower than the cost of commercial adsorbents, such as activated carbon or ion-exchange resins, the prepared biological materials might gain a special attention [6]. Chitin and chitosan have more applications as biopolymers reported for their high potential of adsorption of metal ions [7]. Most adsorbents developed nowadays for the removal of heavy metal ions was based on their interactions with the functional groups on the surfaces of the adsorbents. From these interactions it was concluded that the functional groups present in the adsorbents have important effects on the effectiveness, capacity and reusability for the removal of heavy metal ions [8,9].

Muzzarelli documented that because of the high content of nitrogen on chitosan which acts as an electron donor [10,11] the chitosan exhibited high adsorption capacity for harmful metal ions such as copper, lead, mercury, and uranium from wastewater. Chitosan and its derivates was reported to be an efficient heavy metal scavenger due to its chelating ability [12,13]. The adsorption of the metals on the polymeric backbone was mainly done by the

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secondary bonding interactions like hydrogen bonding, coordinate bonding involving the metal ions and the electron donating groups present at the polymer. The large number of —OH groups plays the metal ion coordination sites in polysaccharides like starch, guargum, xanthan gum etc. In some other polysaccharides like sodium carboxylmethylated cellulose (CMC), sodium alginate and chitosan, apart from —OH groups —COO— (CMC and sodium alginate), $-NH_2$ groups (Chitosan) are present.

These functional groups play an important role for the binding of metal ions. Thus it is possible to develop efficient low cost sorbents for the heavy metals by combining the metal ions attraction capabilities of both the natural polysaccharide and the synthetic polymers.

This can be done by grafting various synthetic polymeric chains of vinyl monomers into the various polysaccharides backbones. Because of instability of chitosan in acidic solutions, cross linking agents like glutaraldehyde [14–16], epichlorohydrin [17] and ethylene glycol diglycidyl ether [18] were used to improve chitosan's durability. Studies on the graft copolymerization of chitosan with various vinyl monomers have been conducted with different initiating systems and different mechanisms [19]. In the present work, using the redox initiator ceric ammonium nitrate, the novel cross linked chitosan graft acrylonitrile copolymer was synthesised. The adsorption behavior of cross linked chitosan graft acrylonitrile copolymer toward Cr(VI), Cu(II) and Ni(II) ions from aqueous solutions was investigated using batch technique. The influence of experimental conditions such as pH, agitation period and adsorbent dose will be studied. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption rates were determined quantitatively and compared by the first- and second-order kinetic model.

2. Materials and methods

2.1. Materials

Chitosan was kindly donated from Indian Sea food, Cochin, Kerala, India was analytical reagent grade. The acrylonitrile monomer and the cross linking agent glutaraldehyde were obtained from Central Drug House Private Ltd, Mumbai. The ceric ammonium nitrate $Ce(NH_4)_2(NO_3)_6$ and nitric acid used was purchased from Thomas Bakers Chemical and Company. All the reagents used were of the analytical grade.

2.2. Preparation of cross linked chitosan copolymer

Chitosan solution was prepared by dissolving 2 g of chitosan flakes in 100 ml of 2% aq. acetic acid solution with constant stirring. To the above prepared chitosan solution about 15 ml of cross linking agent glutaraldehyde was added. This mixture was then stirred well for 20 min using magnetic stirrer. To this cross linked chitosan solution, a known amount of acrylonitrile (1 g in 50 ml of water) was added drop by drop with continuous stirring. Then to initiate the polymerization process in the above mixture a solution of ceric ammonium nitrate (CAN) (0.5 g in 10 ml of 1 N nitric acid) was added. The temperature of reaction was maintained at 70 °C for 45 min. After the completion of addition the product was precipitated by using excess of 2 N sodium hydroxide solution with vigorous stirring. The obtained precipitate was then washed with distilled water several times to remove homopolymer formed. Finally the graft copolymeric product was filtered and dried.

2.3. Polymer characterization

The FT-IR studies of the prepared cross linked chitosan-*g*-acrylonitrile copolymer in solid state was characterized using Perkin–Elmer spectrophotometer with KBr pelletisation in a wide wavelength range between 400 cm^{-1} and 4000 cm^{-1} and X ray diffraction studies were performed using X ray powder diffractometer (XRD–SHIMADZU XD–D1) using a Nifiltered Cu $K\alpha$ X ray radiation.

2.4. Batch adsorption studies

Batch adsorption studies were performed using different concentrations of potassium dichromate, copper sulphate and nickel chloride. The extent of metal ion removal was investigated separately by changing the adsorbent dose, pH of the solution and time of shaking of the adsorbent metal solution mixture. Stock solutions of copper(II) ion was prepared by dissolving $CuSO_4$, that of nickel(II) ion was prepared by dissolving $NiCl_2$ and that of chromium(VI) ion was prepared by dissolving $K_2Cr_2O_7$ in distilled water. The concentration of metal ion solution was 200 mg/l in all three cases.

Batch adsorption experiments were conducted by treating 1 g of cross linked chitosan-*g*-acrylonitrile copolymer with 100 ml of potassium dichromate, copper sulphate and nickel chloride solutions taken in a 250 ml stoppered bottles separately. This solution was then agitated at 30 °C using orbital shaker at fixed speed of 160 rpm. After attaining the equilibrium adsorbent was separated by filtration using Whattman filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer. A similar procedure was carried out at different time intervals, adsorbent doses and pH. The pH of each solution was adjusted to different values using either NaOH or HCl.

3. Results and discussion

3.1. Characterization of the grafted copolymer

3.1.1. FTIR

Fig. 1 shows the FTIR spectrum of (a) cross linked chitosan and (b) cross linked chitosan-*g*-acrylonitrile copolymer. The broad and strong absorption peak at around 3454 cm^{-1} (O—H and N—H stretching), peak at 2923 cm^{-1} (C—H stretching), the three peaks at range of 1000–1157 cm^{-1} (C—O stretching) were common in both spectra (a) and (b) which may be due to the cross linked chitosan backbone. On comparing the FT-IR spectra of cross linked chitosan with the graft copolymer it was observed that the strong peak was obtained at around 2244 cm^{-1} in spectra (b) corresponding to the presence of —CN stretching. The above obtained peak proved the successful graft copolymerization of cross linked chitosan with the acrylonitrile [20].

3.1.2. XRD

The XRD pattern of cross linked chitosan (a) and its graft copolymer (b) was represented in Fig. 2. The cross linked chitosan shows two diffraction peaks at around 11° and 20°. These are characteristics of the hydrated crystalline structure of cross linked chitosan. The peak of (b) obtained at around 42° was due to the overlapped diffraction peaks from the AN's crystal.

While comparing the XRD spectrum of cross linked chitosan with cross linked chitosan-*g*-acrylonitrile, it was observed that diffraction intensity of the peak obtained at around 20° in spectra (b) was obviously weakened. This obtained result indicate that the crystallinity of the cross linked chitosan was found to be decreased after modification. This phenomenon was due to the strong interaction (formation of covalent bond) between cross linked chitosan and acrylonitrile. In other word, copolymerization improved the compatibility between cross linked chitosan and acrylonitrile.