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Synthesis of ethylenediamine modified chitosan microspheres for removal of divalent and hexavalent ions

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ABSTRACT

Ethylenediamine modified chitosan was obtained in the form of microspheres by chemical crosslinking with gluteraldehyde and evaluated for the effective removal of metal ions. The present modification results in additional nitrogen centers which function as potential binding sites and the microsphere form enhances the specific surface area during adsorption of metal ions. The adsorbent was used in batch experiments to evaluate the adsorption of Cu(II), Zn(II), Pb(II) and Cr(VI) in a individual metal salt solutions. The samples exhibited highest affinity for Cu(II) and least for Cr(VI) ions. The adsorption data were interpreted based on Langmuir and Freundlich isotherm models. The maximum adsorption capacity obtained from Langmuir model is 60.9 mg g^{-1}. The modified microspheres can be regenerated with high efficiency, suggesting that this adsorbent is satisfactory to reuse.

1. Introduction

Environmental pollution has always been a serious issue, especially regarding heavy metal ions. Unlike some organic pollutants, heavy metals are considered to be the most dangerous polluting agents in water. The danger is due to their bioaccumulation and non-biodegradability and can exist for a long time in natural environment [1].

The amount of heavy metals produced from metal industries, agricultural activities and waste disposal has been increased dramatically. If the level of metal ions is beyond the tolerance limit, it will cause serious environmental and public health problems. As a consequence, the development of the effective techniques for the removal of toxic metal ions from waste water is very important for the remediation of water pollution.

A variety of solid supports including polymeric resins and inorganic materials have served as selective sorbent platform for the removal of metal ions [2]. Up to now numerous technologies has been developed for the removal of metal pollutants from liquid waste. These include methods such as chemical precipitation [3], electrodialysis [4], electroplating, ion-exchange [5], membrane process, biosorption [6] and so on. Each method has its inherent limitation such as incomplete removal of metal ions and limited tolerance to pH change [7].

The chelating properties of molecules are utilized for water treatment and particularly to recover metals [8]. Several such studies have been reported in the literature on the enhancement of adsorption ability of chitosan and adsorption selectivity [9–11]. The application of biopolymers as adsorbents is an emerging technique and is of interest in studies on the removal of metal ions from aqueous solutions. Adsorption is versatile and effective method for removing toxic metal ions particularly when it is combined with appropriate regeneration step. This reduces the problem of sludge disposal and renders the system economically viable.

Chitosan is one of the most abundant natural polysaccharide and well known for its biocompatible and biodegradable properties. It was reported that chitosan, because of its high amino content has found to posses good sorptive capacity for many heavy metal ions [12], through complexation of a metal ions with the amino group of chitosan. The free amino function of chitosan gives it a better ability to chelate ions of transition metals than other natural polymers such as cellulose and its derivatives [13].

Recently, there has been a growing interest in the chemical modification of chitosan in order to improve its solubility and widen its applications [14–16]. Chitosan has two types of reactive groups that can be grafted. First, the free amine groups on deacetylated units and secondly, the hydroxyl groups on the C_3 and C_6 carbons on acetylated or deacetylated units. Recently researchers have shown that after primary derivation followed by graft modification, chitosan would obtain much improved water solubility, antibacterial

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and antioxidant properties [17,18]. Grafting chitosan is also a common way to improve other properties such as increasing chelating [19] or complexation properties [20].

The high sorption capacities of modified chitosan for metal ions can be of great use for the recovery of valuable metals or the treatment of contaminated effluents. A great number of chitosan derivatives have been obtained with the aim of adsorbing metal ions by including new functional groups onto the chitosan backbone. The grafting of sulphur and nitrogen compounds on chitosan has been the subject of many studies for the design of chelating chitosan-based resins [21–23]. The present investigation deals with chemical modification of chitosan by incorporating the ethylene-1,2-diamine moiety as pendent chain covalently binded to the main polymeric frame work. These basic nitrogen centers can adsorb cations from the aqueous solution and anions from the acidic solution by complexation. The possibility of obtaining the modified chitosan in the form of microspheres has been investigated. The microspheres have been evaluated for removal of few bivalent and Cr (VI) from metal salt solutions.

2. Instrumentation

The infrared spectra of the compounds were recorded on a IR-Prestige-21, FTIR spectrometer (Shimadzu, Japan). Samples were prepared as KBr pellets and scanned in the range 4000–400 cm^{-1}. Scanning electron micrographs (SEM) of the samples before and after adsorption of metal ions were recorded on a JEOL-JSM 5800LV scanning electron microscope under a voltage of 20 kV. The concentration of divalent metal ions in aqueous solutions were determined in mg L^{-1} using Atomic Absorption Spectrometer, GBC932 plus, calibrated with standard metal ion solutions. The concentration of Cr(VI) in aqueous solutions were determined in mg L^{-1} using Shimadzu UV-2550 (Japan) UV–vis Spectrophotometer calibrated with standard Cr(VI) solution.

2.1. Materials and reagents

Materials Chitosan (Cts) molecular weight is 1.9×10^5–3.1×10^5 based on viscosity was purchased from Sigma–Aldrich(India). Phthalic anhydride (Pth), N,N-dimethylformamide (DMF), N-Bromosuccinimide (NBS), Triphenylphospine (TPP), Liquid Paraffin, Gluteraldehyde, Ethylene-1,2-diamine(En), Hydrazinehydrate, N-methyl-2-pyrrolidone (NMP), Potassium dichromate ($K_2Cr_2O_7$), Diphenyl carbazide, Acetic acid, Copper sulphate, Lead nitrate, Nickel sulphate, Zinc sulphate, Sodium hydroxide and hydrochloric acid were all reagent grade and purchased from Spectrochem (India).

2.2. Synthesis

2.2.1. Synthesis of N-phthaloylchitosan (PtCts)

Phthaloyl chitosan was synthesized according to a previous method [24]. A sample of 1.0 g Cts was reacted with 4.04 g of Pth in 20 mL of DMF/water (95/5) at 120 °C with stirring under nitrogen. The mixture turned into a viscous dispersion in about 1.5 h and then to a gelatinous mass in 2 h. The reaction was continued and after 8 h, the mixture was cooled to room temperature and the product was precipitated in 500 mL of ice water. The solid product, represented as PtCts, was washed with methanol and dried to give 1.62 g (90%) of white powdery material.

2.2.2. Synthesis of N-bromo phthaloylchitosan (PtCtsBr)

3.4 g of PtCts was dispersed in 337 mL of NMP and 20.5 g of NBS and 30.3 g of TPP were added to an ice bath, and the mixture was heated to 80 °C and stirred for 2 h under nitrogen atmosphere. The reaction mixture was poured into ethanol; the precipitate was filtered, washed with ethanol and dried at 40 °C under vacuum.

2.2.3. Synthesis of ethylene-1,2-diamine-6-deoxy-N-phthaloylchitosan (PtCtsEn)

A sample of 1 g of PtCtsBr was dispersed in 50 mL of DMF and stirred for 2 h at 80 °C on a water bath. 5 mL of En was added and the mixture was maintained at 80 °C. After 2 h, the mixture was cooled to room temperature, the product, designated as PtCtsEn, was filtered, washed with water and dried.

2.2.4. Synthesis of ethylene-1,2-diamine-6-deoxy-chitosan(CtsEn)

A sample of 0.21 g of PtCtsEn was dispersed in 15 mL of NMP. To the mixture 15 mL of aqueous hydrazine monohydrate (4 M) was added, and the mixture was stirred at 100 °C for 4 h under nitrogen. The product, designated as CtsEn, was filtered, washed with alcohol and dried.

2.2.5. Preparation of gluteraldehyde crosslinked ethylene-1,2-diamine-6-deoxy-chitosan in the form of microspheres (CtsEn microspheres)

To obtain the CtsEn in the form of microspheres (Scheme 1.), 2.0 g CtsEn was dissolved in 10 mL of 1% (v/v) acetic acid solution. The mixture was agitated for 5 min. The resulting viscous mass was emulsified by vigorous stirring in a mixture containing 80 mL liquid paraffin containing 0.15 g span-80 at room temperature. After 30 min, about 2.5 mL of 25% (v/v) aqueous glutaraldehyde solution was added. Stirring was continued for 1 h, to obtained CtsEn in the form of microspheres. It was separated by filtration, washed with petroleum ether followed by acetone to remove the adhering liquid paraffin and unreacted gluteraldehyde. Microspheres were dried at 60 °C.

2.3. Adsorption and desorption studies

2.3.1. Adsorption studies

The capacity of CtsEn microspheres to adsorb copper (Cu), lead (Pb), zinc (Zn) and hexavalent chromium Cr(VI) ions from aqueous solution was determined in duplicate using a batch process. About 10 mg of CtsEn microspheres were suspended in 25.0 mL of an aqueous metal salt solution with concentrations of each metal ion varying in the range 5–20 mg L^{-1}. After 2 h the suspensions were centrifuged. Aliquot of the supernatant was appropriately diluted and concentration of the divalent metal ions and hexavalent chromium ions was estimated using AAS and UV–visible spectrophotometer respectively. The amount of hexavalent chromium ion was estimated by absorbance measurements at 540 nm using diphenyl carbazide as the complexing agent.

The absorption capacity of CtsEn was determined using the following equation.

$$q_e = \frac{(C_o - C_e)V}{W}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}); C_o and C_e are the initial and equilibrium liquid phase solute concentrations (mg L^{-1}) respectively; v is the liquid phase volume (L) and w is the amount of the absorbent (g).

2.3.2. Desorption studies

To evaluate the reusability of CtsEn microspheres as sorbent material, adsorption experiments were followed by desorption. The adsorption experiments were carried out by suspending about 10 mg of CtsEn in 25 mL of Cr(VI) metal ion solution of initial concentration 40 mg L^{-1}. After 1 h, the Cr(VI) adsorbed sample was separated by centrifugation, washed with water and dried. For

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