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Chitosan-alginate nanoparticles (CANPs) as potential nanosorbent for removal of Hg (II) ions

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ABSTRACT

Chitosan-alginate nanoparticles were prepared using microemulsion method for removal of Hg (II) ions from aqueous solutions and optimization was done in terms of two biopolymers, crosslinker concentrations. Plausible interactions between the material and Hg(II) ions were explored after adsorption and explained by characterizing by various techniques such as Fourier transform infrared (FTIR) spectroscopy, Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), Scanning electron microscopy(SEM), Particle size and Zeta-potential measurements. The adsorption capacity was evaluated by studying various parameters such as the effect of pH (optimum value 5 for adsorption and 1 for desorption), contact time (optimum value 90 min), adsorbent dose (optimum value 200 mg), initial metal ion concentration (optimum value 4 mg/L) and temperature (optimum value 30 °C). The maximum adsorption capacity of CANPs for Hg (II) was found to be 217.39 mg/g at 30 °C which is claimed to be one of the exceptionally obtained highest values reported in the literature so far. The equilibrium sorption data were fitted satisfactorily to the Langmuir adsorption model with R^2 value of 0.96054. The progress of adsorption process was found to follow the second order kinetics. The results obtained in this study proved that the prepared biopolymer nanomaterial could be an effective and economically viable adsorbent for removal of Hg (II) ions. Moreover, the nanoparticles can be regenerated and reused subsequent for the metal removal.

1. Introduction

Chitosan (poly–β–(1 → 4)–2–amino–2–deoxy–D–glucose) is a hydrophilic, nontoxic, biodegradable, and biocompatible material showing affinity to form complexes with metal ions (Rinaudo, 2006; Zhang and Cui, 2012) due to the presence of amino groups which interact with metal ions through ion exchange or chelation. The high content of amino groups also facilitates chemical modifications of this biopolymer to improve its adsorption features, such as selectivity and adsorption capacity (Sampaio Caroline de et al., 2015). Its adsorption performance can further be improved by cross-linking with reagents such as glutaraldehyde, tripolyphosphate salts, epichlorohydrin, ethylene glycol or diglycidyl ether, which stabilize chitosan in acid solutions and enhance its mechanical properties also (Radwan et al., 2010). Alginate is another natural polysaccharide extracted from brown seaweeds. It is a linear polymer is composed of β-D-mannuronate and ά-L-guluronate units linked by β-1,4 and ά-1,4 glycosidic bonds and has a capacity to remove toxic pollutants (Douglas and Tabrizian, 2005).

Chitosan and alginate have been separately investigated as adsorbents for metal ions like Cu(II), Cd (II), Pb(II), Ni(II), Hg(II), Cr(VI), U(VI), Mo(V), V(V), Pd(II), Pt(IV), Au(III), As(V), Se(V) showing high adsorption capacities (Zhou et al., 2009). The maximum adsorption capacity depends on factors such as the forms of chitosan and alginate (beads, powder), chemical modifications (cross-linking, grafting reactions), different experimental conditions (pH, particle size, conditioning, and composition of the solution) (Kyzas and Deliyanni, 2013).

In general, contamination of aquatic systems is a serious environmental global problem caused by the pollution of natural waters by heavy metal ions. Mercury is one of the most toxic known heavy metals since it is non biodegradable and produces a lot of toxic effects in the human body (Pillai et al., 2009). Its presence is due to the combination of natural processes (volcanic action, erosion of mercury–containing sediments) and anthropogenic activities (mining operations, tanneries, metal plating facilities) as well (Rocha et al., 2009). In the present work Hg (II) was selected as toxic metal ion for removal using batch adsorption technique which is considered to be one of the most effective and economical

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treatment methods for removal of metal ions in the area of separation processes (Dai et al., 2012). Although numerous works have been published aiming the removal of various metals or especially Hg (II) by adsorption onto either chitosan or alginate based materials (Jeon and Park, 2005; Vieira et al., 2011; Vieira and Beppu, 2006), however, blending of these two biopolymers after crosslinking with tripolyphosphate and calcium chloride, respectively is still not attempted. Modified chitosan and alginate for the removal of some metal ions are reported in literature; however, there is lack of studies which use chitosan-alginate powders (nanomaterials) (not resins or membranes) as adsorbent for removal of mercury (II) ions from aqueous solution.

Thus, the objectives of the present study include to (a) prepare novel chitosan-alginate nanoparticles (CANPs) with large porosity, surface area, (b) characterize the CANPs by FTIR, TEM and SEM/EDX techniques, (c) investigate the effects of pH, initial ion concentration, temperature, contact time adsorbent dose on adsorption and subsequent removal of Hg (II) and fitting the obtained adsorption data to adsorption isotherms and kinetic models. The novelty of the work lies in the fact that the biopolymers used are fully biodegradable and nontoxic and, therefore, the disposal of the adsorbents is no longer a problem. Moreover, due to cationic and anionic nature of chitosan and alginate, they have potential to adsorb both anionic and cationic type of toxic metal ions, respectively.

2. Experimental

2.1. Materials

Chitosan and alginate were procured from Merck, India and used without further treatment. Sodium tri-polyphosphate and calcium chloride (Dihydrate) obtained from Loba Chemie, Mumbai, India, were used as crosslinking agents for chitosan and alginate, respectively. Liquid paraffin oil (Marck, India) was used as an oil phase to prepare microemulsion. Other chemicals such as mercury chloride ($HgCl_2$) (adsorbate), rhodamine B(indicator), ammonium thiocynate, were used of high purity grade. Doubly distilled water was used throughout the experiments.

2.2. Characterization of CANPs

Prior to using the prepared adsorbent for adsorption experiments, the adsorbent was characterized by the following techniques:

2.2.1. Fourier transforms infrared (FTIR) spectroscopy

The FTIR spectra of prepared adsorbent (CANPs) was recorded on a FTIR spectrophotometer (8400, Shimadzu). Samples for the spectral analysis were prepared by mixing adsorbent and KBr in 1:10 proportion and the spectra were obtained in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}.

2.2.2. Transmission electron microscopy (TEM)

The morphologies of the adsorbents, on different magnifications were recorded using the Transmission electron microscopy (TEM) (Morgagni-268-D transmission electron microscope) with an acceleration voltage of 80.0 kV. The sample for the TEM measurements was prepared by dispersing a drop of the sample solution on carbon coated copper grid and then the excess fluid on the surface was removed with a filter paper and the sample was air-dried before TEM examination.

2.2.3. Size distribution and zeta potential measurements

The size of nanoparticles and their zeta potentials were measured using a Zetasizer (Malvern Instrument, Malvern, UK). All experiments were done in triplicate.

2.2.4. SEM/EDX analysis

A scanning electron microscope with an electron dispersive X-ray spectrometer (SEM/EDX, JEO, JSM-5800LV) was used to study the surface morphologies and elemental analysis of the Hg (II) adsorbed CANPs.

2.3. Preparation of chitosan-alginate nanoparticles (CANPs)

In order to prepare CANPs the microemulsion method was adopted (Gupta and Karar, 2011). In brief, an aqueous phase was prepared by dissolving 1.0 g chitosan and 1.0 g alginate in 2% acetic acid solution and 100 mL hot water, respectively. While for preparing the oil phase paraffin oil was used. The above three solutions were mixed with vigorous shaking (Shaking speed 1000 RPM, 5 L capacity, Remi, India) for 30 min to form a stable emulsion and after that 10 mL of 1 M sodium tri-polyphosphate and 10 mL of 1 M calcium chloride solutions were added as crosslinkers with constant stirring and the crosslinking reaction was allowed to take place for 3 h at room temperature. The nanoparticles formed were cleaned by washing them thrice with acetone and the prepared CANPs were stored in air tight polyethylene bags.

2.4. Preparation of synthetic adsorbate solution

Standard mercury (II) stock solution of 1000 mg/L was prepared by dissolving 1.3535 g of $HgCl_2$ (Merck India Ltd) in 1000 mL of distilled water. The stock solution was further diluted with deionized water to obtain the desired concentration solutions for further experiments.

2.5. Adsorption experiments

The adsorption experiments were carried out using the batch contact method as reported in the literature (Hossain et al., 2012). In brief, 0.1 g of CANPs was added in to a 10 mL of $HgCl_2$ solution at constant pH and temperature. The mixture was shaken on a thermostat shaker (Rivotech, India) for 90 min to attain equilibrium at room temperature. After shaking was over, the suspension was centrifuged (Remi, India) and the amount of adsorbed Hg (II) was measured spetrophotometrically following the rhodamine B method published elsewhere (Ramakrishna and Aravamudan, 1976).

The absorbed amount and the% removal of Hg (II) were calculated by the following equations,

respectively.

$$\text{Adsorbed amount}\left(\text{mg/g}\right) = \frac{C_i - C_f}{m}V \quad (1)$$

$$\%\text{Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i is the initial and C_f is the final concentration of metal ion solutions (mg/L), respectively, V being the volume of adsorbate solution; and m the weight of adsorbent (CANPs).

3. Results and discussion

3.1. FTIR spectral analysis

FTIR spectra of native chitosan, alginate, prepared CANPs and Hg(II) adsorbed CANPs were recorded as shown in Fig. 1(a)–(d),