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Chitosan/sporopollenin microcapsules: Preparation, characterisation and application in heavy metal removal

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ABSTRACT

Use of natural polymers as biosorbents for heavy metal removal is advantageous. This paper reports a study aiming to design a novel biosorbent from two biomacromolecules; chitosan, a versatile derivative of chitin, and sporopollenin, a biopolymer with excellent mechanical properties and great resistance to chemical and biological attack. Chitosan/sporopollenin microcapsules were prepared via cross-linking and characterised by employing scanning electron microscopy, Fourier transform infrared spectroscopy and thermogravimetric analysis. Sorption performance of the microcapsules and the plain chitosan beads were tested for Cu(II), Cd(II), Cr(III), Ni(II) and Zn(II) ions at different metal ion concentration, pH, amount of sorbent, temperature and sorption time. The adsorption pattern followed Langmuir isotherm model and the sorption capacity of the chitosan/sporopollenin microcapsules was found to be Cu(II): 1.34, Cd(II): 0.77, Cr(III): 0.99, Ni(II): 0.58 and Zn(II): 0.71 mmol g^{-1}. Plain chitosan beads showed higher affinity for the ions; Cu(II): 1.46, Cr(III): 1.16 and Ni(II): 0.81 mmol g^{-1} but lower for Cd(II): 0.15 and Zn(II): 0.25 mmol g^{-1}. Sporopollenin enhanced Cd(II) and Zn(II) ions sorption capacity of the chitosan microcapsules. Chitosan/sporopollenin microcapsules can be used in Cd(II) and Zn(II) metal removal.

1. Introduction

Water bodies are contaminated with heavy metal ions through discharge of waste from many industries such as metal plating, mining, textile and electric/electronic devices manufacturing [1,2]. The waste effluents from these industrial operations, untreated or even treated, can have significant amounts of heavy metal ions. Heavy metal ions in aquatic systems and ground water pose risks to the living organisms by accumulating in food chain due to their mobility, stability and non-biodegradability [3]. When their detrimental effects and toxicity are considered, it is critical to remove heavy metal ions to save diminishing water resources.

There have been increasing interest and efforts to improve conventional techniques to treat the metal contaminated effluents efficiently. Among the conventional physicochemical methods, adsorption has been extensively employed because of its ease of use, effectiveness and feasibility [1,4].

Selection of sorbent is a key parameter when sorbents for heavy metal removal are designed. In addition to physicochemical characteristics of a sorbent such as its selectivity towards certain species and sorption capacity, its cost and production procedures should be assessed. Many materials with natural or artificial origin such as activated carbon, resins, fly ash, oxides, silicates, clays, zeolites, pine bark and cotton waste have been used as adsorbents and reported in the literature [5,6]. These studies on sorbents have demonstrated the need for more efficient, inexpensive and renewable adsorbents. Bio-based sorbents can fulfil these needs; biomaterials are abundant in nature, and also many functional groups for metal interaction are present on them or they can be easily functionalised.

Chitin, a carbohydrate with nitrogen content, is the second most abundant biopolymer in the biosphere. Chitosan, a derivative of chitin produced via deacetylation of chitin in high alkaline conditions, is a biocompatible and biodegradable [7,8] polymer with high affinity for metal ions [8,9]. The alkaline hydrolysis of chitin exposes free amino groups ($-NH_2$) and gives the polymer unique cationic nature [10]. The pendant amino groups of chitosan are primary cause of its higher metal ion sorption capacity and its solubility in aqueous solutions when compared to chitin. Amino and hydroxyl groups (especially at the C-3 position) on chitosan can serve as electrostatic interaction and complexation sites for metal cations [11,12]. This makes chitosan an appropriate sorbent in heavy metal

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uptake [13]. Many workers have opted for chitosan composites as sorbent and prepared chitosan composites from natural products [14,15]. However, preparation of a chitosan-based biosorbent with sporopollenin has not been reported in the literature.

Sporopollenin is a natural biomacromolecule present in the outer wall (also called exine) of spores and pollens. This polymeric material is highly resistant to chemical and biological attack and can retain its morphology in geological strata over millions of years [16,17]. Many analytical techniques have been performed to reveal its chemical nature; however, information available on its chemical structure is still limited and needs clarifying. Nevertheless, some studies indicated that sporopollenin is mainly an aliphatic polymer with phenolic and aromatic groups or conjugated side chains [18]; it is considered as a macromolecule composed mainly of carotenoid and carotenoid esters [19].

Sporopollenin particles extracted from *Lycopodium clavatum* (common club moss) has excellent mechanical strength and are reasonably monodisperse [20]. Recently, Fraser et al. (2014) reported that sporopollenin from *L. clavatum* is also resistant to heat and its chemistry does not alter until a threshold of 250–300 °C [21]. Many researchers have appreciated the unique nature of the sporopollenin and have conducted works with raw or functionalised form of it including metal removal studies [22–25].

Once dissolved in acidic solutions, chitosan can be transformed into insoluble gel form via cross-linking; giving the polymer structural stability in acidic media. Cross-linking also enables incorporation of fine particles into the polymeric matrice. Cross-linking forms three dimensional sites within the networks; enhancing the metal uptake [26]. Preparation of chitosan composite sorbents from different sources has been reported earlier. Glutaraldehyde, which forms Schiff bases with amines, is one of the cross-linking agents used in synthesis and modification of these chitosan-based adsorbents [27].

In this paper, we describe the preparation of a novel bio-based adsorbent combining physicochemical properties of both chitosan and sporopollenin. The synthesised microcapsules were characterised by employing scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). We attempted to provide insights into how heavy metal ions; Cu(II), Cd(II), Cr(III), Ni(II) and Zn(II), interact with chitosan/sporopollenin microcapsules and the cross-linked chitosan beads without sporopollenin. Also, we tried to compare the metal ion uptake capacities of the sorbents. The microcapsules exhibited higher efficiency over the chitosan beads. Sporopollenin grains entrapped in the chitosan polymeric matrice significantly improved the metal ion capture capacity of the microcapsules. The chitosan/sporopollenin microcapsules can be used in treatment of the waters contaminated with heavy metal cations.

2. Experimental

2.1. Materials

Medium molecular weight chitosan was obtained from Sigma–Aldrich. Sporopollenin from *L. clavatum* with 20 μm particle size was purchased from Fluka Chemicals. Metal salts ($Cu(NO_3)_2{\cdot}3H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}4H_2O$) were purchased from Merck, $Cd(NO_3)_2{\cdot}4H_2O$ was obtained from Sigma–Aldrich. Glutaraldehyde (25% in water, v:v) was obtained from Merck. Double distilled water purified with Barnstead (Dubuque, IA) ROpure LP® reverse osmosis system was used in the experiments.

2.2. Preparation of chitosan/sporopollenin microcapsules

Preparation of chitosan/sporopollenin microcapsules was carried out as follows: Chitosan solution was prepared by dissolving 3.00 g chitosan in 150 mL of acetic acid solution (2% v/v). The mixture was continuously stirred for 20 h. Subsequently, 1.500 g of sporopollenin particles was added into the chitosan solution and then the mixture was stirred for 3 h until homogeneity. The chitosan/sporopollenin mixture was transferred into a burette. This mixture was dropped into the coagulation solution (a mixture of 200 mL of water, 300 mL of methanol and 60.0 g NaOH [28]). Resulting microcapsules were incubated in the coagulation solution for 24 h to achieve a complete gelation, giving a yellow-brownish colour to the medium. Then, the microcapsules were recovered and rinsed thoroughly with distilled water until the filtrate was of neutral pH and free of coloured decomposition products of the sporopollenin grains. Wet microcapsules (otherwise they could not retain their spherical shape when dried) were recovered by filtration and transferred into cross-linking reaction solution (0.9 mL of glutaraldehyde solution in 90 mL of methanol). The cross-linking solution was refluxed at 70 °C for 6 h. Finally, cross-linked microcapsules were recovered and washed thoroughly first with ethanol and then with water to remove any unreacted glutaraldehyde molecules. The cross-linking treatment and the following washing steps were performed in a fume hood to arrest any glutaraldehyde vapour. The microcapsules were allowed to dry at room temperature. Plain chitosan beads were synthesised following the same method but without adding sporopollenin grains to the chitosan solution.

2.3. Microcapsule characterisation and analytical methods

The surface morphology of chitosan/sporopollenin microcapsules were investigated with Scanning electron microscope (EVO LS 10 ZEISS). FT-IR spectra of chitosan/sporopollenin microcapsules were obtained with a Perkin Elmer 100 FT-IR Spectrometer 2.5. Thermogravimetric analysis of chitosan/sporopollenin microcapsules were done with a Setaram Thermogravimetric Analyzer/Setsys (EXSTAR S11 7300). Metal ion concentration in the solutions was determined using a flame atomic absorption spectrophotometer (Contr AA 300, Analytik jena).

2.4. Metal sorption experiments

Metal sorption studies were done as follows: 0.1500 g of the sorbent (chitosan/sporopollenin microcapsules or plain chitosan beads) was placed into 25 mL of metal ion solution and agitated for 4 h at 200 rpm. Then, the sorbent was filtered through a filter paper. The effects of amount of sorbent (0.0500–0.2500 g), contact time (60–480 min.), metal ion solution pH (3.0–5.8), initial metal ion concentrations (2–12 mg/L) and temperature (25, 35 and 45 °C) on sorption behaviour of the microcapsules and the chitosan beads were studied. The amount of metal ions adsorbed by the sorbent was determined from the difference of metal concentrations in the initial and final solutions employing following equation below:

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where q_e is the metal sorption capacity of the microcapsules or chitosan beads (mmol g^{-1}), C_i and C_e are the initial and equilibrium liquid-phase concentrations of metal ions (mmol L^{-1}), respectively; V is the volume of metal solution (L), and W is the mass of the sorbent interacted with metal ion solution in grams.

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