



Research paper

Ultrasound assisted preparation of chitosan–vermiculite bionanocomposite foams for cadmium uptake



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ABSTRACT

The objective of this work was the development of functional bionanocomposites based on the intercalation of the cationic biopolymer chitosan in natural or in organically modified vermiculite samples under experimental conditions involving ultrasound irradiation. The resulting materials were processed as macroporous foams with the aim to apply them in the removal of Cd(II) ions from aqueous solution. Physicochemical characterization confirmed the intercalation of chitosan into the interlayer space of vermiculite, causing the exfoliation of VU layers in those bionanocomposites. They were processed as foams by means of freeze-drying resulting in materials that show interconnected elongated macropores with average diameter around 150–200 μm, and the material in the cell walls exhibited a tendency to organize in parallel planes. The adsorption equilibrium data of Cd(II) on the bionanocomposite foams, carried out in batch mode, was interpreted with the Langmuir, Freundlich and Prausnitz–Radke (P–R) isotherm models, and the P–R isotherm showed the best fit to the experimental data. The adsorption capacity was increased by raising the solution pH, which most likely favors a chelation mechanism between the chitosan chains and the Cd(II) cations. The chitosan–vermiculite bionanocomposites with the highest chitosan content showed exceptionally high adsorption capacity values, at least three times higher than those of the individual components.

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1. Introduction

Currently, bionanocomposites represent a remarkable type of nanostructured hybrid materials with new structural and functional properties, obtained through the combination of natural polymers (biopolymers) and inorganic solids with at least one dimension at the nanometer scale (Ruiz-Hitzky et al., 2008a, 2008b). Applications of bionanocomposites encompass food packaging, flame retardancy purposes, components in optics, electric and electrochemical devices, as well as biomedicine (Darder et al., 2007). Bionanocomposites can be prepared using a wide variety of inorganic solids, including silica, hydroxyapatite and other calcium phosphates, calcium carbonates, α-zirconium phosphate, layered perovskites, metallic and metal oxide nanoparticles, carbon nanotubes, laminar clays (smectites) and their alkylammonium derivatives, and layered double hydroxides (LDHs) (Ruiz-Hitzky et al., 2005, 2008b; Coradin et al., 2006; Aimé and Coradin, 2012; Shchipunov, 2008; Shchipunov et al., 2009; Ojijo and Ray, 2013).

Among them, natural and modified clays have been commonly applied to prepare bionanocomposites because of their high availability and significant understanding about their intercalation chemistry (Pavlidou and Papaspyrides, 2008).

Among the biopolymers present in nature, chitosan has been extensively used in synthesis of bionanocomposites due to its availability and interesting properties. It is one of the most abundant polysaccharides on earth, obtained by basic deacetylation of chitin present in insects and sea crustacean shells (Agboh and Qin, 1997). Chitosan is being applied as adsorbent since the amino groups in its structure can interact with cationic metal species through chelation or ion exchange mechanisms (Dzul Erosa et al., 2001). However, this use as an adsorbent has been limited because of chitosan solubility in water, especially under acidic conditions, which affects its mechanical properties. Its assembly to inorganic solids such as clay minerals can improve the structural properties and increase its resistance in aqueous media. The properties of the bionanocomposites are highly dependent on the interaction type between the chitosan and the clay mineral. Thus, the search for materials with high affinity between both components is an ongoing challenge. Smectites and fibrous clay minerals like sepiolite have been combined with chitosan to produce bionanocomposites for various applications

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(Darder et al., 2003, 2005, 2006; Zia et al., 2011; Liu et al., 2011; Wang et al., 2005; Xu et al., 2006; Zuber et al., 2010; Alcántara et al., 2014). For instance, those materials resulting from the intercalation of chitosan into sodium montmorillonite were applied as active phase in sensors for potentiometric determination of anions (Darder et al., 2005). Other applications of these materials include their use as membranes for gas separation (Choudhari and Kariduraganavar, 2009) or as adsorbents of diverse pollutants such as organic species and heavy metal ions (An and Dultz, 2007, 2008). However, very few studies have addressed the preparation of chitosan bionanocomposites based on vermiculite (Zhang et al., 2009). Vermiculite is a 2:1 phyllosilicate, generally trioctahedral with Mg^{2+} ions in octahedral sites and isomorphic substitution of Si^{4+} by Al^{3+} , that shows a superior layer charge than smectites (>0.6 per formula unit) and therefore elevated cation exchange capacity (greater than 100 meq/100 g) (Grim, 1968; Brigatti et al., 2006). Among other applications, vermiculites have been employed within the field of environmental remediation, being successfully utilized for the removal of Mn(II), Cd(II), Cu(II), Pb(II), Ni(II), Zn(II), Co(II), Cr(III), Fe(II), Al(III), Ca(II) and Mg(II) because of its high cation exchange capacity (CEC) (Blais et al., 2003; Das and Bandyopadhyay, 1991; da Fonseca et al., 2005, 2006; Malandrino et al., 2006; Vieira dos Santos and Masini, 2007; Padilla-Ortega et al., 2014). Various studies have shown that the adsorption mechanism of cations on vermiculite is governed by cation exchange, and electrostatic interactions with the aluminol and silanol groups present at the edges of the silicate layers (Malandrino et al., 2006). However, access of polymers to the inter-layer space of vermiculite is strongly limited due to its high charge density per unit cell that restrains the entry to that region, and so the synthesis of nanocomposites based on vermiculite intercalation is difficult, representing nowadays a challenge in the topic of polymer-clay nanocomposites.

The aim of the current work was to optimize the synthesis of bionanocomposites based on chitosan and vermiculite, prepared from the natural clay or from an organovermiculite obtained by treatment of vermiculite with hexadecyltrimethylammonium bromide. The bionanocomposites were synthesized in aqueous medium homogenizing the systems by ultrasound irradiation, followed by processing of the resulting materials as low density macroporous foams. The bionanocomposites were characterized by diverse physicochemical techniques including CHN chemical analysis, TG and DTA thermal analysis, X-ray diffraction, FTIR spectroscopy and electronic microscopies (TEM and FE-SEM). Textural properties (specific surface area, mean pore diameter and pore size distribution) were analyzed from N_2 BET adsorption-desorption isotherms and macroporosity of foams was analyzed by Hg porosimetry and microtomography. Additionally, the removal of Cd(II) from water solution by the bionanocomposites was investigated to elucidate the adsorption mechanism, and to evaluate the effect of chitosan/clay ratio on the Cd(II) adsorption capacity of the bionanocomposites. The Cd(II) was chosen as a model cationic metal, but it also could be of practical interest because it is the second most-toxic heavy metal, so its presence in aqueous effluents poses an extreme danger to the environment.

2. Experimental section

2.1. Materials

Vermiculite used in this work, designated as VU, was supplied by Virginia Vermiculite company, USA, and its characteristics have been recently reported (Padilla-Ortega et al., 2014). The cationic surfactant hexadecyltrimethylammonium (HDTMA) chloride, chitosan (designated as CHT, corresponds to medium molecular weight, between 190,000 and 310,000 Da, 75–85% deacetylated), NaOH, nitric acid and cadmium nitrate were supplied by Sigma-Aldrich. Acetic acid was obtained from Merck. Deionized water (resistivity of 18.2 M Ω cm) was obtained with a Maxima Ultrapure Water from Elga.

2.2. Preparation of organovermiculite

The VU was modified by adsorbing the cationic surfactant HDTMA, and the modified vermiculites are referred as organovermiculite (OVU). The modification procedure is described as follows. A certain volume of a solution of HDTMA with an initial concentration of 100 mmol/L and a given mass of the VU were added to an Erlenmeyer flask. The concentration of VU in the suspension was 2% w/w. The flask was placed in a constant temperature water bath at 30 °C, and the VU suspension was continuously stirred during seven days. The OVU was then separated from solution and washed several times with deionized water to remove the residual surfactant. It was finally dried at ambient temperature for 24 h and stored in a closed container.

2.3. Synthesis of the chitosan-vermiculite bionanocomposites

The CHT solutions with concentrations ranging from 0.5 to 10 g/L were prepared by dissolving CHT in 1% w/w acetic acid solution, and the solution pH was adjusted to 5. A portion of 15 mL of CHT solutions was slowly added to 15 mL of 4% w/v VU or OVU suspensions, and kept under magnetic stirring for 2 h at 50 °C. For maximum dispersion of the solid in the CHT solution, the samples were sonicated with an ultrasonic cell disrupter (Sonics, Vibracell VC740, operated at 20 kHz). A total energy of 15 kJ was applied in intermittent pulses of 10 s followed by 10 s in standby. Afterwards, the mixture was kept under magnetic stirring at 50 °C for three days. The solid was separated by centrifuging the samples and stored at -15 °C overnight. The CHT concentration in the remaining solution was analyzed using a total organic carbon (TOC) analyzer (Analytik Jena AG, Multi N/C 2100). Finally, the frozen solid was lyophilized in a freeze-dryer (Cryodos -80 , Telstar) to produce the bionanocomposite foams.

The bionanocomposites were labeled based on the used clay, VU or OVU, and the initial amount of CHT expressed as weight percentage of the total solid content (10, 18, 31, 50, 57, 65 and 69% CHT w/w). For example, VU50%CHT represents a bionanocomposite prepared by using vermiculite VU and a suspension of CHT leading to a theoretical weight percentage of 50% CHT.

2.4. Characterization of the chitosan-vermiculite bionanocomposites

The chitosan content in the samples was quantified by an elemental analyzer CNHS/O (Perkin-Elmer 2400). X-ray diffraction analysis (Bruker D8) was employed to corroborate the presence of intercalated species in vermiculite. Infrared spectra (IR) were obtained using an Attenuated Total Reflectance (ATR) equipment (Shimadzu, IRAffinity-1, GladiATR10). The morphology of the materials surface was examined by an optical microscope (Motic, SMZ-168), as well as by means of a FE-SEM equipment FEI-NOVA NANOSEM 230, which allows direct observation of the samples adhered on a carbon tap without requirement of any conductive coating on the surface. TEM images were obtained in a Philips Tecnai 20 microscope operating at 200 kV. The true density, ρ_s , was determined with a He pycnometer (UltraFoam™1200e, Quantachrome Instruments). Compression modulus of the VU65%CHT foam was evaluated with an Instron Universal Testing Machine, Model 3345 (Instron Engineering Corporation), using cube shaped samples (width about 13 mm and height about 8 mm), and the crosshead speed was set at 5 mm min^{-1} . Textural properties were determined by a N_2 physisorption and porosimetry analyzer (Micromeritics, ASAP 2010). Macroporosity of the foams was characterized by means of mercury intrusion porosimetry (Quantachrome Instruments, Poremaster Series) and X-ray microtomography, using a high resolution SkyScan 1272 X-ray microtomograph. The X-ray source voltage and current used are 20 kV and 175 μA , respectively. The nominal resolution is 2.25 μm using the X-ray detector of 2452×1640 pixels. NRecon software (v. 1.6.9.8, SkyScan) was used to reconstruct cross-section images from microtomography projections to 3D images, using Feldkamp algorithm. The

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