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Research paper

Preparation and characterization of the eco-friendly chitosan/vermiculite biocomposite with excellent removal capacity for cadmium and lead

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ABSTRACT

The chitosan/vermiculite biocomposite (CTS-VMT) was synthesized successfully with epichlorohydrin (ECH) cross-linking agent and used to remove cadmium and lead from the aqueous solution. CTS-VMT was characterized by FTIR, SEM, BET, TG-DTG, zeta potential and XPS. The effects of critical parameters including solution pH, contact time, initial heavy-metal concentration and adsorbent regeneration were investigated. Besides, adsorption mechanisms were also researched. The results indicated that chitosan molecule cannot intercalate into the interlayer space but cross link on the external surface of VMT. The maximum adsorption capacities for Cd(II) and Pb(II) were 58.48 mg g^{-1} and 166.67 mg g^{-1} at pH 4, respectively. The adsorption process fitted well the pseudo-second-order model and the adsorption isotherms could be correctly simulated by the Langmuir isotherm model. The zeta potential analyses put forward that electrostatic attraction existed in the adsorption process between the metal cations and CTS-VMT. However, the principal mechanism for adsorption on CTS-VMT was chelation according to the kinetic study and XPS analyses. Moreover, the desorption experiments revealed the prepared adsorbent tended to be regenerated by using HCl and the removal rations for four cycles were all > 90%. Therefore, the synthesized CTS-VMT in this study has the potential to be utilized as an eco-friendly adsorbent for removing Cd(II) and Pb(II).

1. Introduction

Heavy-metal contamination has already attracted extensive attention owing to its voluminous discharge, high toxicity and non-biodegradability. Industrial wastewaters deriving from the fertilizers, fungicides, metal fabrication, paints, pigments and batteries are the potential origin of heavy metal ions. Cadmium and lead are widespread in the environment and harmful to the human beings. Nowadays, several techniques such as adsorption, ion exchange, chemical precipitation, membrane separation and reverse osmosis have been applied to remove the toxic metal ions from industrial effluents (Naushad et al., 2014; Karthik and Meenakshi, 2015; Zhang et al., 2016b). Among all the mentioned techniques, adsorption is regarded as one of the most promising approach for the remediation of heavy metal contaminated (Zhang et al., 2016b). However, the selection of adsorbent is especially important, which directly affects the adsorption capability and economic performance during the adsorption process. Besides, conventional adsorbents have several defects such as low efficiency, costly and environmentally harmful, etc. Hence, it is of greatly practical significance to investigate the high-efficiency, inexpensive and eco-friendly adsorbent.

Currently, biocomposites based on biopolymers and clay minerals, which are low cost, biocompatibility, biodegradability and highly efficient, have attracted consideration attention accounted to their unique functional properties and structure (Zhong et al., 2012; Zafar et al., 2016; Bensalem et al., 2017). Chitosan (CTS) is an exuberant biopolymer produced by alkaline *N*-deacetylation of chitin that is the second most plentiful biopolymer in nature. Chitosan possesses special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity and excellent adsorption capacity, etc. Therefore, chitosan is accounted as an ideal natural absorbent results from the presence of amine ($-NH_2$) and hydroxyl (−OH) groups (Wan Ngah et al., 2011;

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Ngwabebhoh et al., 2016). However, its disadvantages (such as low acid stability, low thermal stability and inadequate mechanical strength) confine the application of chitosan (Zhang et al., 2016b). To overcome the defects of chitosan, the combination between chitosan and inorganic solids has aroused the interest of the researchers.

Crude clay minerals are widely found in nature and have the characteristics of low-cost and outstanding adsorption performance (Tirtom et al., 2012). It would be much more expensive if we use chitosan alone in preparation of adsorbent compared to the chitosan biocomposites based on clay mineral. Therefore, the compound of chitosan with clay mineral cannot only overcome the defects of chitosan, but also reduce costs and broaden the appliance of adsorbent in industry. Especially, the biocomposites based on both chitosan and montmorillonite have been widely utilized in the field of environmental remediation, being triumphantly exploited to remove Pb(II), Cu(II), Co (II), Cr(VI), Ni(II), Cd(II), Cs(I), As(V) and Pd(II) (Cho et al., 2012; Tirtom et al., 2012; Pereira et al., 2013; Wang et al., 2014; Liu et al., 2016b; Yang et al., 2016). Vermiculite (VMT), a 2:1 mica-type phyllosilicate, presents more exchanged cations than montmorillonite and therefore has the superior cation exchange capacity owing to the isomorphic substitution of Si^{4+} by Al^{3+}. Furthermore, its expansibility is less than smectite due to their higher charge in the tetrahedral sheets (Malandrino et al., 2006). Hence, vermiculite is suitable to use as an excellent adsorbent. However, very little attention has been devoted to the preparation of chitosan/vermiculite biocomposites. Several researchers had investigated chitosan/vermiculite bionanocomposite in the application of heavy metal removal, for example Cd (II) (Padilla-Ortega et al., 2016), As(III) (Saleh et al., 2016), Cr(VI) (Prakash et al., 2015), and so on. Nevertheless, to the best of our knowledge, few chitosan/vermiculite bionanocomposite were prepared by crosslinking, especially using epichlorohydrin (ECH) as crosslinking agent. ECH is a crosslinking mono-functional agent that was used to form covalent bonds with the carbon atoms of the hydroxyl groups of chitosan, resulting in the rupturing of the epoxide ring and the removal of a chlorine atom (Tirtom et al., 2012; Guan et al., 2016). As the crosslinking agent, epichlorohydrin can improve chemical stability, mechanical resistance, pore size and adsorption/desorption properties (Jawad and Nawi, 2012).

In the present study, we prepared a novel type the chitosan/vermiculite biocomposite (CTS-VMT), which were prepared with epichlorohydrin (ECH) as a cross-linking agent. The structural properties of CTS-VMT were further studied by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), Thermogravimetric (TG) and zeta potential. The characteristics of adsorption towards Cd(II) and Pd(II) onto the CTS-VMT, including effect of solution pH, contact time, initial concentration and adsorbent regeneration were investigated systematically. In addition, the adsorption mechanism was further analyzed by X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

The raw vermiculite was purchased from Sigma-Aldrich. The chemical composition (wt%) of VMT was as follows: SiO_2 42.99%, MgO 19.46%, Al_2O_3 11.26%, Fe_2O_3 11.02%, K_2O 5.92%, CaO 2.50%, MnO 0.087%, Na_2O 0.030%. The cation exchange capacity (CEC) of VMT was 0.852 meq g^{-1}. Chitosan (80.0–95.0% deacetylation degree, viscosity 50–800 mPa s) was obtained from Shanghai Titan Scientific Co. Ltd. Epichlorohydrin was provided by Aladdin Chemistry Co. Ltd. The other chemical reagents including sodium tripolyphosphate, $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, NaOH, HNO_3 (65% wt%) and acetic acid were all analytical grade and supplied by Guangzhou Chemical Reagent Factory (Guangzhou, P.R.C). All reagent solutions were prepared with deionized(DI) water.

2.2. Preparation of chitosan-vermiculite biocomposite

The chitosan/vermiculite biocomposite was prepared as following: Firstly, powdered chitosan (1.0 g) was completely dissolved in 100 mL 2.0% (v/v) acetic acid to obtain chitosan viscous solution. Secondly, specific amounts of vermiculite were dispersed in the above viscous solution by ultrasonication for an hour, and then the mixture was stirred for 2 h until it was homogeneous. Thirdly, the homogeneous and stable chitosan/vermiculite solution was dropped slowly into 100 mL sodium tripolyphosphate solution (5.0 wt%) by a peristaltic pump under constant stirring for 4 h to obtain the initial product. The initial product was filtered and washed by deionized water until pH = 7.0. Finally, 250 mL 0.1 mol L^{-1} NaOH and 3.14 mL epichlorohydrin (ECH) were simultaneously added into the system containing the initial product and maintained at 50 °C for 2 h. Thereafter, crosslinked chitosan-vermiculite composite was collected by centrifugation and washing several times with distilled water. The final products were dried at 60 °C until constant weight and pulverized to pass through a 200-mesh sieve, which denoted as CTS-VMT. The CTS-VMT was for further use. Fig. 10 shows the structure of the new adsorbent (CTS-VMT) formed by hydrogen bonding interaction, electrostatic incorporation interaction and covalent crosslinking interaction. For comparison, materials with different CTS/VMT mass ratio followed similar methods by adding different concentration of raw material.

2.3. Characterization of chitosan-vermiculite biocomposite

The Fourier transform infrared (FTIR) spectra were analyzed by KBr pellet technique in the spectral range of 4000–400 cm^{-1} with 4 cm^{-1} resolution, using a PerkinElmer 1725X FTIR spectrometer. The SEM images of samples were investigated by a ZEIZZ Merlin Scanning electron microscopy (SEM, Carl Zeiss, Germany). The specific surface areas were carried out utilizing the Brunauer-Emmett-Teller method. Thermogravimetric analysis(TG) of materials were performed by using Netzsch STA 409 PC/PG instrument with a heating speed of 10 °C min^{-1} from room temperature to 800 °C under N_2 atmosphere. The zeta potentials were measured at different pH values (2, 4, 6, 8 and 10) by using Zeta size Nano ZS (Malvern Instruments, UK). XPS analyses were operated on the X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Scientific Escalab, USA).

2.4. Batch experiments for heavy metal ion adsorption

The adsorption solutions of Cd(II) and Pb(II) were obtained by diluting 1000 mg L^{-1} standard stock solutions which were prepared by dissolving $Cd(NO_3)_2.4H_2O$ and $Pb(NO_3)_2$ in deionized water, respectively. The pH of the solution was adjusted to 4.0 with negligible volume of 0.1 M HNO_3 and NaOH by applying pH meter (PHS-2, Three Letters Instrument Factory, Shanghai). The batch experiments were conducted by equilibrating 0.04 g adsorbent with 20 mL heavy metal solution (including Cd(II) or Pb(II)) in a temperature-controlled rotary shaker at 30 °C for 24 h. The supernatant was collected by centrifuging and then filtered by 0.45 μm cellulose membranes after adsorption equilibrium. The concentration of Cd(II) or Pb(II) in the samples was calculated by ICP-MS (Agilent, 7700, USA). The effect of adsorbent dosage (0.5–4 g L^{-1}), pH (1.5–8 for Cd(II) and 1.5–5 for Pb(II)), contact time (1–1400 min) and initial concentration (25–300 mg L^{-1} for Cd(II) and 50–500 mg L^{-1} for Pb(II)) were investigated to optimize the adsorption reaction conditions. The adsorption capacity and the removal rate of adsorbent for metal ions were obtained according to the following equations (Paulino et al., 2011):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

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