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Adsorptive removal of Lead from water by the effective and reusable magnetic cellulose nanocomposite beads entrapping activated bentonite

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ABSTRACT

Many efforts have been driven to decontaminate the drinking water, and the development of efficient adsorbents with the advantages of cost-effectiveness and operating convenience for the removal of Pb^{2+} from water is a major challenge. This work was aimed to explore the possibility of using cellulose-based adsorbents for efficient adsorption of Pb^{2+}. The millimeter-scale magnetic cellulose-based nanocomposite beads were fabricated via an optimal extrusion dropping technology by blending cellulose with the carboxyl-functionalized magnetite nanoparticles and acid-activated bentonite in NaOH/urea aqueous solution, and then they had been tested to evaluate the effectiveness in the removal of Pb^{2+} from water. The effects of contact time, initial heavy metal ion concentrations, adsorption isotherms and solution pH on the sorption behavior were studied. The thermodynamic parameters (ΔG, ΔH and ΔS) indicated that the adsorption processes were feasible, spontaneous, endothermic and mainly controlled by chemical mechanisms. The reusability of the adsorbent was also studied.

1. Introduction

Lead (Pb^{2+}) has been recognized as one of the most toxic metals (Mehdipour, Vatanpour & Kariminia, 2015). With the rapid growth of urbanization and industrialization, Pb^{2+} released into ecosystem has been one of serious environmental concerns (Kul & Koyuncu, 2010b), which may cause severe health problems in vital organs of humans (Nordberg, Fowler & Nordberg, 2014). Limitations to the availability of clean water are recognized currently as a global human health threat. At the current growth rates, the population will be consuming 90% of the available fresh water by 2025 (Ayoub, Venditti, Pawlak, Salam & Hubbe, 2013). As almost all countries in the world strive to reduce levels of elevated blood Pb in children, accurate quantification of Pb risks from potable water taps in individual homes will become of greater concern (Clark, Masters & Edwards, 2014). Owing to the fact, the removal of Pb^{2+} from drinking water (surface water and groundwater) is critical in terms of protection of public health and environment. Many efforts have been driven to decontaminate the drinking water, but the need for an efficient, cost-effective, robust, and handy technology for the decontamination of downstream water without endangering human health is still tremendous. The application of conventional removal techniques was restricted by their high costs or ineffectiveness in the case of low concentration of Pb (Aragay, Pons & Merkoçi, 2011), while adsorption is a convenient process for this case. Some effective adsorbents have been continuously developed and improved, including activated carbon (Murugesan et al., 2014), zeolites (Borhade, Kshirsagar, Dholi & Agashe, 2015), clay minerals (Jiang & Liu, 2014), and chitosan (Luo, Zeng, Liu & Zhang, 2015; Najafabadi, Irani, Rad, Haratameh & Haririan, 2015). However, there are also some shortcomings associated with these adsorbents, such as high costs, difficulties in separation, and/or necessity for regeneration systems of secondary wastes. Therefore, there is an increasing interest in developing more effective, renewable and low-cost absorbents. Recently, numerous approaches have been studied for the development of cheaper and more effective natural polymers-based adsorbents for their being widely available and eco-friendly (Crini, 2005). Cellulose is the most abundant renewable polysaccharide on earth with very attractive properties, such as biocompatibility, biodegradability, and thermal and chemical stability. The utilization of cellulose as bioaffinity carrier materials should enhance the adsorption capability of organic wastes by virtue of the coupling route between abundant hydroxyl groups

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and heavy metal ions (Crédou & Berthelot, 2014; Singha & Guleria, 2014). However, the application of native cellulose was limited by not enough adsorption capacity. Inorganic nanoparticles/cellulose composite materials are a good candidate absorbent for this case. Adsorption of leads by cellulose-based composites will be a very complex process, in which there are several mechanisms including complexation, coordination, chelation, ion exchange, adsorption by physical forces and ion entrapment in inter- and intra-fibrillar capillaries and spaces of the cellulose matrix network.

Currently, magnetic adsorbents have emerged as a new generation of materials for environmental decontamination. Especially, superparamagnetic iron oxide nanoparticles are highly apposite to environmental remediation due to their large surface area, surface modifiability, biocompatibility, low toxicity and chemical inertness (Neyaz, Siddiqui & Nair, 2014). The clay minerals have potential applications as low-cost and efficient adsorbents of Pb^{2+}. Bentonite is mainly composed of montmorillonite, which is a 2:1-type aluminosilicate with net negative charge on the clay surfaces (Akcil, Erust, Ozdemiroglu, Fonti & Beolchini, 2015). Treatment of bentonite with concentrated inorganic acids can replace exchangeable cations with H^+ ions and induce the release Al^{3+} and other cations out of both tetrahedral and octahedral sites. As a result, enhanced mesoporosity with the important textural and structural changes (Eren, Afsin & Onal, 2009; Koyuncu & Kul, 2014; Kul & Koyuncu, 2010b) is produced to increase the adsorption capacity.

In this work, magnetic cellulose-based nanocomposite beads (MCNB) were designed by incorporating cellulose with carboxyl-functionalized Fe_3O_4 nanoparticles (MN-CA) and acid-activated bentonite (AAB) via an optimal extrusion dropping technology. The kinetics, equilibrium and thermodynamic of adsorption, the influences of solution pH, reusable property, and adsorption mechanisms were investigated in the removal of Pb^{2+} ions from water.

2. Experimental

2.1. Materials

Cotton linter pulp (α-cellulose >95%) was provided by Hubei Chemical Fiber Group Ltd. (Xiangfan, China). Its viscosity-average molecular weight (M_η) was determined by viscometry in cadoxen to be 12.5×10^4 Dalton (Cai, Liu & Zhang, 2006). The Fe_3O_4 nanoparticles powder (I109514, 99.5%, 20 nm) was purchased from Aladdin industrial corporation (Shanghai, China). Bentonite (285234, powder, 400 mesh) was purchased from Sigma-Aldrich. A stock solution of Pb^{2+} was prepared by dissolving required amount of $Pb(NO_3)_2$ (Merck) in double distilled water at room temperature. The stock solutions were then diluted in double distilled water to get various initial concentrations, which was calibrated by an atomic absorption spectroscope (AAS, SOLAAR M6, Thermo, USA). Other chemicals used were of analytical grade, and were purchased in China.

2.2. Preparation of MCNB

The carboxyl decorated magnetite (Fe_3O_4) nanoparticles (MN-CA) were obtained by post-modification of the magnetite surface with citric acid following the reported procedure (Chen, Gao & Ni, 2008). The magnetic nanoparticles were added to 0.1 M citric acid with ultrasonic treatment for 30 min and then the reaction was maintained for 4 h at room temperature. The MN-CA was isolated with a magnet and washed several times with water and acetone.

The acid-activated bentonite (AAB) was carried out using a Pyrex glass reactor with reflux condenser (Kul & Koyuncu, 2010b). 50.0 g raw bentonite was slowly added to 250 mL 14 M HCl solution, stirred and maintained at boiling point temperature (approximately 378 K) for 4 h. The reaction products were filtered and washed 5 times with distilled water to remove traces of acid. After each wash Cl^- was detected with silver acetate solution.

MCNB were prepared by an optimal extrusion dropping technology as our previous work (Luo & Zhang, 2009). A green mixture solvent (the mixture of NaOH/urea/H_2O of 7:12:81 by weight) was cooled to $-12\,^\circ C$ (Cai et al., 2007), and then 8.0 g cellulose was immediately dispersed into the solvent (200 mL) under vigorous stirring for 3 min to obtain a transparent cellulose solution. 0.5 g of MN-CA and 6.0 g of AAB powder were added into the cellulose solution with mechanical agitation for 1 h and then with ultrasonic homogenization 3 times for 5 min to obtain the composite cellulose solution. The resulting solution was added drop wise in 10 wt% sodium chloride bath by the means of a syringe pump. Without stirring, spherical beads were yielded when the drop was set at 6 cm in height from the bath. Afterwards, the composite beads were washed several times with distilled water and then kept in water before characterization. The resultant beads were stored in water for adsorption experiments or freeze-dried for 48 h in a freeze drier for sample characterization.

2.3. Characterization

The composite beads prepared were observed with a digital camera (Canon A630). The image analysis software was used to analyze the mean diameter and size distribution of composite beads. The magnetic properties of the magnetite and MCNB were studied with a superconducting quantum interference device (SQUID, MPMS XL-7, QUANTUM DESIGN, USA) at $25\,^\circ C$, and the hysteretic loop was obtained in a magnetic field that varied from −7 to +7 T. The surface and cross section structure of the beads were observed with a FESEM scanning electron microscopy (SEM, SIRION TMP, FEI). Samples were ground into powders and dried in a vacuum oven at $60\,^\circ C$ for 48 h for other characterization. Fourier-transform infrared spectra were recorded on an FTIR spectrometer (model 1600, Perkin-Elmer Co.). X-ray diffraction (XRD) analysis was carried out with an XRD diffractometer (D8-Advance, Bruker). Thermo gravimetric analysis (TGA) was carried out on thermo gravimetric analyzer (TA Inst, model SDT Q600).

2.4. Kinetics study

A series of conical flasks (100 mL) containing 30 mL Pb^{2+} solutions (120 mg L^{-1}) were kept in a thermostatic shaking water bath at different temperatures (298 K, 303 K and 313 K). 5.0 g of the wet MCNB was added to each conical flask, and then shaked mechanically at 250 rpm. At given time intervals, the beads were removed with a magnet and the resultant solutions were analyzed for Pb^{2+} using AAS.

2.5. Adsorption isotherms study

For isotherms studies, a series of conical flasks (100 mL) containing 30 mL Pb^{2+} solutions in the concentration range of 60–160 mg L^{-1} were kept in a thermostatic shaking water bath at different temperatures (298 K, 303 K and 313 K). 5.0 g of the prepared MCNB was added to each conical flask vibrated mechanically at 250 rpm for 3 h. The beads were removed with a magnet and the resultant solutions were analyzed for Pb^{2+} using AAS.

2.6. Regeneration experiments

To study the recyclability, the previously used MCNB was regenerated in the 2 mol L^{-1} sodium citrate. After elution, the MCNB beads were rinsed three times with deionized water to remove any