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Efficient Pb(II) removal using sodium alginate–carboxymethyl cellulose gel beads: Preparation, characterization, and adsorption mechanism

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ABSTRACT

Alginate–carboxymethyl cellulose (CMC) gel beads were prepared in this study using sodium alginate (SA) and sodium CMC through blending and cross-linking. The specific surface area and aperture of the prepared SA–CMC gel beads were tested. The SA–CMC structure was characterized and analyzed via infrared spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Static adsorption experiment demonstrated that Pb(II) adsorption of SA–CMC exceeded 99% under the optimized conditions. In addition, experiments conducted under the same experimental conditions showed that the lead ion removal efficiency of SA–CMC was significantly higher than that of conventional adsorbents. The Pb(II) adsorption process of SA–CMC followed the Langmuir adsorption isotherm, and the dynamic adsorption model could be described through a pseudo-second-order rate equation. Pb(II) removal mechanisms of SA–CMC, including physical, chemical, and electrostatic adsorptions, were discussed based on microstructure analysis and adsorption kinetics. Chemical adsorption was the main adsorption method among these mechanisms.

1. Introduction

Toxic metal pollutants, such as lead, exist widely in industrial wastewater (i.e., battery, electroplate, dye, and pigment production) (Gautam, Mudhoo, Lofrano, & Chattopadhyaya, 2014; Martín-Lara, Blázquez, Ronda, Rodríguez, & Calero, 2012; Subhashini, Velan, & Kaliappan, 2013; Wei et al., 2014). Given the natural physiological toxicity and non-biodegradability of lead, this material easily accumulates in biological bodies and causes various diseases even at low concentrations (Villa, Peixoto, & Cadore, 2014; Wu, Deng, Lin, & Tsai, 2013; Zhou, Fu, Zhang, & Levit, 2014). Common lead processing methods are costly. In terms of cost and efficiency, adsorption is a promising processing technique for wastewater with low lead concentration (Gollavelli, Chang, & Ling, 2013; Gupta, Verma, Khan, & Verma, 2013; Hadi, Barford, & McKay, 2013; Wu, Wei, & Zhang, 2011).

Sodium alginate (SA), which is a natural polysaccharide, mainly comprises β–D–M (mannuronic acid) and α–L–G (guluronic acid), and contains many free carboxyl groups ($-COO^-$). As a polymeric flocculant with high adsorption capacity, SA can react with many divalent and trivalent cations (i.e., Ca^{2+}, Ba^{2+}, and Fe^{3+}) to produce a stable gel (Chen et al., 2010; Davis, Kalis, Pinheiro, Town, & van Leeuwen, 2008; Mandal & Ray, 2013; Papageorgiou et al., 2012). Researchers have reported that SA can effectively eliminate heavy metal ions, such as Pb^{2+}, Cu^{2+}, and Cd^{2+} (Bertagnolli, da Silva, & Guibal, 2014; Lagoa & Rodrigues, 2009; Lim, Zheng, Zou, & Chen, 2008; Papageorgiou, Kouvelos, & Katsaros, 2008). However, SA is limited by poor stability (Liu et al., 2013), weak water resistance, and serious thermal degradation (Phang, Chee, Lee, & Teh, 2011). Therefore, SA requires modification before used to process heavy metal ions in wastewater. Common modifications include oxidation, hydrophobic modification, esterification, and graft copolymerization.

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Sodium carboxymethyl cellulose (CMC) is a kind of high-polymer cellulose ether (Pushpamalar, Langford, Ahmad, & Lim, 2006; Yaşar, Toğrul, & Arslan, 2007) CMC is an anionic high-molecular compound obtained from the reaction of natural cellulose with caustic alkali and acetic acid. Numerous carboxyls and hydroxyls exist in the macromolecular chain of CMC. These compounds can produce hydrogels with a 3D cross-linked structure by coordinating with multivalent cations, such as Fe^{3+} and Al^{3+} (Mohamed, 2012). Both SA and CMC are natural polymers. These polymers are characterized by rich sources; water solubility but organic solvent insolubility; simple molding; excellent biodegradability, biocompatibility, and bioactivity; and environment friendliness (Abdel-Halim & Al-Deyab, 2011; Falamaki, Naimi, & Aghaie, 2006; Reis et al., 2009; Vijaya, Popuri, Boddu, & Krishnaiah, 2008).

SA and CMC have been extensively studied recently. However, studies on the preparation, microstructure, and adsorption mechanism of SA–CMC gel beads are rare. Based on previous experimental studies, Tulika Dewangan et al. prepared SA–CMC gel beads using $CaCl_2$ (Dewangan, Tiwari, & Bajpai, 2010; Dewangan, Tiwari, & Bajpai, 2011). The authors analyzed the adsorption of the prepared SA–CMC gel beads to a series of heavy metal ions, and they discussed the influence of temperature, pH, and reaction time on the adsorption performance. However, the authors did not analyze the microstructure, adsorption mechanism, and internal causes of removing heavy metal ions using SA–CMC gel beads. Experiments showed that the extensive use of SA–CMC gel beads is difficult because of their poor mechanical strength.

Based on previous experimental studies, SA–CMC–Ca–Fe gel beads (hereinafter referred to as SA–CMC gel beads) were prepared in the present study by cross-linking and beading SA and CMC in $CaCl_2$ and $FeCl_3$ solutions. The preparation involved different SA and CMC mass ratios. The SA–CMC gel beads improved the performance of a single component, enhanced mechanical strength, and lowered SA cost. The structure of the prepared SA–CMC gel beads was characterized and analyzed through surface and aperture analyses, infrared spectroscopy (IR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Pb^{2+} adsorption and related influencing factors were also discussed based on these analyses. The adsorption mechanism was explored through kinetic and structural analyses. The results of this study could lay a solid foundation to develop new bio-based adsorbing materials.

2. Materials and methods

2.1. Materials

SA (analytical grade, viscosity ≥0.02 pa.s under 10 g/L concentration and 20 °C), CMC (analytical grade, viscosity ≥0.3–0.8 pa.s under 20 g/L concentration and 25 °C), $FeCl_3$ (analytical reagent (AR), and $Pb(NO_3)_2$, (AR) were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd. (Beijing, China). $CaCl_2$(AR) was provided by Tianjin Bodie Chemical Co., Ltd. Pb(II) stock solution (1000 mg /L) was prepared by dissolving lead nitrate in deionized water. Working solutions were prepared through progressive dilution of the stock Pb(II) solution.

2.2. Preparation of SA–CMC dispersion

Different amounts of SA (1.0, 0.5, 0.33, 0.25, and 0.20 g) were dissolved in 40 mL of distilled water to produce a viscous solution after stirring at 20 °C. Different masses of CMC (0, 0.5, 0.67, 0.75, and 0.80 g) were then added into the corresponding SA solution under constant stirring to generate a homogeneous dispersion. The different combinations of SA and CMC data see supplementary Table 1.

2.3. Preparation of SA–CMC gel beads

Under magnetic stirring, the mixture solution was dropped into 100 mL of 1% $CaCl_2$ solution using a 10 mL syringe, and the solution was sealed in the shade to solidify (24 h). The coagulated beads were then washed several times with distilled water and placed in 100 mL of 1% $FeCl_3$ solution to further solidify (24 h). Finally, the SA–CMC gel beads were washed several times with distilled water and then air-dried at 20 °C. The cross-linking degree of SA–CMC gel beads measured using the tea bag method (Mahdavinia, Pourjavadi, & Zohuriaan-Mehr, 2004; Pourjavadi, Barzegar, & Mahdavinia, 2006). Its mean swelling capacity is 1.73 g/g. An image of the SA–CMC is presented in the Supporting Information (Fig. S1).

2.4. Preparation of the traditional adsorbent

Pretreatment of cation exchange resin: A certain amount 0.8 g of 732 cation exchange resin was collected, rinsed with distilled water, and soaked in anhydrous ethanol for 4 h for the resin to fully expand to remove impurities, namely inorganic impurities (mainly iron compounds) and organic impurities (unreacted monomer, low-molecular polymer, breakdown products of resin, ect.), which characterized the solution becoming colorless and the pH equaling 7, and the removed percentage of every impurities including inorganic and organic was more than 99.5 wt %. Subsequently, the resin was washed with distilled water until ethanol was eliminated with measurement the refractive index of the solution equals 1.3333, the same as water. The resin was soaked in 2 wt.% HCl for 24 h. Finally, the resin was washed with distilled water and air-dried at 20 °C.

Pretreatment of granular activated carbon: The particle size of activated carbon between 60 and 80 mesh was filtered. The weight is 0.8 g which mesh 60 of activated carbon accounts for most, about 90%. The activated carbon was oven-dried for 3 h at 105 °C. The final humidity was below 2%. The dried activated carbon was then stored in a desiccator.

2.5. Structural characterization and performance test of SA–CMC gel beads

The specific surface area and aperture were tested through vacuum N_2 adsorption using a V-Sorb 2800P specific surface area and aperture distribution tester (Beijing Gold Spectrum Technology Co., Ltd.). The samples were activated and vacuumed under 200 °C until reaching at least 0.3 Pa vacuum degree prior to the test. The Fourier transform infrared (FTIR) spectra of the prepared SA–CMC gel beads were obtained by a BRUKER TENSOR 27 infrared spectrometer (BRUKER Co.) using the KBr compression technique within the wavelength range of 400–4000 cm^{-1}. The microstructure of the prepared SA–CMC gel beads was observed using a JSM-6380A SEM (JEOL) under electron beam acceleration voltage of 20 kV. The SA–CMC gel beads were magnified 25 and 500 times. EDS characterization of the prepared SA–CMC gel bead surfaces was further analyzed using the same JSM-6380A SEM under electron beam acceleration voltage of 15 kV and 15 mm WD. Each sample was tested three times. The percentage of each element in every sample was considered the mean of the three tests. pH of solution was measured by PHS-25 pH meter (ShangHai INESA Scientific Instrument Co., Ltd.); Refractive index of solution was tested through WAY-2S type Abbe refractometer (ShangHai Optical Instrumental Factory). All data analyzed in the test were normalized.