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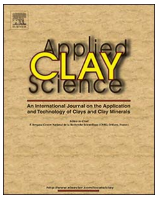

Research paper

The modification of rectorite with carbon layers and trisodium trimetaphosphate for the removal of Pb^{2+}

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ABSTRACT

At the presence of rectorite (Rec), starch was treated with hydrothermal carbonization to fabricate carbon layer with many oxygen containing groups on the surface of Rec layer, which were further reacted with trisodium trimetaphosphate (STMP) to introduce phosphate ester groups on Rec. The obtained RecCPN were used to remove heavy metal ions from aqueous solution. The adsorption kinetics and isotherms could be described with the pseudo- second-order model and the Langmuir model. The maximum monolayer adsorption capacities could reach 258.40 mg/g for RecCPN at pH 5 and 303 K, in which the Pb^{2+} adsorption processes was spontaneous. The positive values of ΔH^0 indicated that the interaction of Pb^{2+} with phosphate ester groups was endothermic. RecCPN still exhibited the good adsorption capacity in the adsorption-desorption cycles. In addition, RecCPN showed advantageous selectivity towards Pb^{2+} over other metal ions (Cu^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+}) and still removed above 90% Pb^{2+} at the initial trace Pb^{2+} concentration (0.5 mg/L).

1. Introduction

Rectorite (Rec) is an interstratified clay mineral, which alternately consists of non-expansible dioctahedral mica-like layers and expansible dioctahedral smectite-like layers with 1:1 ratio (Lu et al., 2014). The interlayer cations in the smectite-like layers can exchange with cations, which make Rec become a good adsorbent for the removal of cationic pollutants such as Pb(II) (Mei et al., 2015; Feng et al., 2016), Hg(II) (Ghasemi et al., 2012), Cu(II), Cd(II) (Li et al., 2013), Sr(II) (Zhao et al., 2014) and NH_4^+ (Zheng and Wang, 2009), and organic dyes (acid red, neutral red and methylene blue) (Wu et al., 2011; Feng and Xu, 2013). Since Rec structure can easily cleave between smectite-like interlayers, Rec layers can be intercalated or exfoliated by large volumes of exchange groups to obtain the large specific surface area.

As the carrier, Rec could be loaded with natural polymers to introduce new functional groups. Polymer can be intercalated into the interlayer space of Rec to enhance its interlayer distance (Xie et al., 2015). Chitosan is made up of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit). The functional groups (the amino group at 2-site and hydroxyl group at 6-site) could be served as the coordination sites for adsorption of toxic heavy metal (Wu et al., 2010). Zeng et al. (2015) prepared cross-linking chitosan/rectorite microspheres to remove Cd (II), Cu(II) and Ni(II) from water. Three-dimensional (3D) architectures of Rec were investigated as the adsorbents. Cationic guar gum (CGG) was attached to Rec by using a cationic-exchange reaction. CGG was regarded as a physical crosslinker to consolidate the 3D Rec layer networks (Zheng et al., 2013), which exhibited high adsorption capacity for ethanol, oil and stearic acid. Chitosan was intercalated into Rec, and then chitosan was crosslinked with glutaraldehyde to form 3D interconnected networks (Lu et al., 2015). The calcination process burnt away the polymer components to eliminate the resistance of chitosan for the adsorption of cationic methylene blue. However, the selective adsorption and the adsorption capacity were still not satisfied for the adsorbents on the base of Rec. More endeavors need to be devoted to the improvement of adsorption capacity, competitive adsorption and trace adsorption to explore the application on the removal of cationic pollutants.

Starch could form the good interaction with Rec (Chang et al., 2012), and the oxygen-containing functional groups could be produced on the surface of hydrothermal carbon from starch (Cui et al., 2006). In this work, starch as the carbon source was compounded with Rec to

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prepare carbon layers onto the surface of Rec. The carbon layers contained a large number of oxygen-containing groups, which could react with trisodium trimetaphosphate (STMP) to introduce phosphate ester groups on the Rec/carbon nanocomposites. As it is well known that phosphate ester groups could form the chelation with metal ions, Pb^{2+} was chosen as the model compound of heavy metal ions to evaluate the adsorption capacity of the modified Rec/carbon nanocomposites. In the nanocomposites, phosphate ester groups, the residual oxygen-containing groups (non-reaction with STMP) and Rec layers could all contribute to the removal of Pb^{2+} from water.

2. Experimental

2.1. Materials

Sodium rectorite was provided by Hubei Zhongxiang Rectorite Mine (Wuhan, China). Potato starch was purchased from Manitoba Starch Products (Manitoba, Canada). All other reagents were of analytical grade and commercially available.

2.2. Preparation of Rec/Carbon nanocomposite (RecCN)

RecCN was fabricated with the hydrothermal method (Feng et al., 2016). 3.2 g rectorite was added in 100 mL distilled water with ultrasonication for 10 min. 2.5 g potato starch was gelatinized at 90 °C for 30 min. 20 mL Rec/starch paste was mixed with 10 mL $(NH_4)_2Fe(SO_4)_2$ solution (0.2 mmol/L) in a Teflon-lined stainless steel autoclave (50 mL), and heated at 180 °C for 12 h. The obtained RecCN were centrifuged, washed with water, and oven-dried at 70 °C for 6 h.

2.3. The modification of RecCN with trisodium trimetaphosphate (STMP)

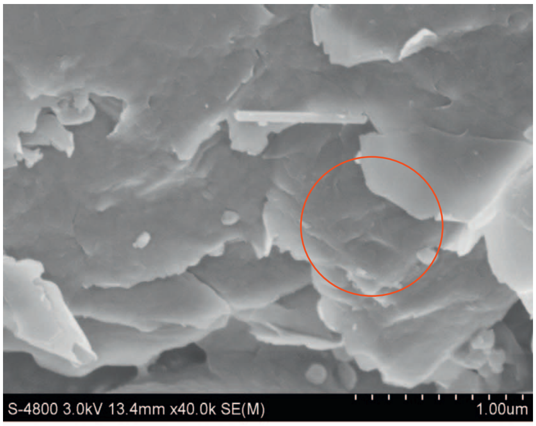
STMP (0.05, 0.1, 0.2 or 0.3 g) was respectively added in 100 mL NaOH solution (3%) with vigorous stirring. 0.2 g RecCN was immersed, and the reaction was processed at 30 °C for 2 h. The modified RecCN were washed in water several times, and then washed with ethanol three times. The products were dried for testing. The modified RecCN with different mount of STMP were respectively labeled as RecCP1N, RecCP2N, RecCP3N and RecCP4N.

2.4. Characterization

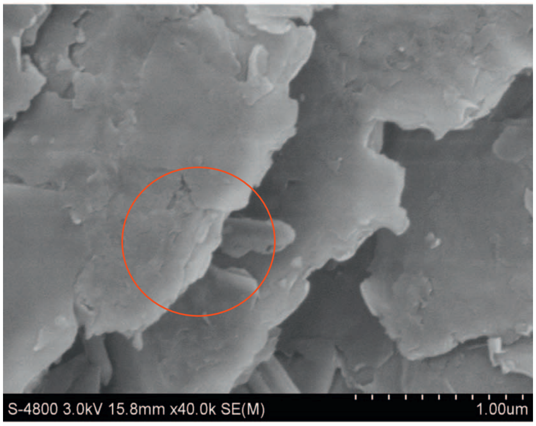
The surface morphology of Rec, RecCN and RecCP2N were observed with an S-4800 scanning electron microscope. In order to determine the composition, RecCP2N powders were tested with a JEM-2100F transmission electron microscope, and displayed in energy dispersive spectroscopic mapping with a JEM-2100F transmission electron microscope. X-ray diffraction patterns were recorded to characterize the changes of the interlayer space in reflection mode with a D/MAX-2500 at a CuKα wavelength of 1.542 Å. FTIR spectra of Rec, RecCN and RecCP2N were performed on a BIO-RAD FTS3000 IR spectra scanner to identify the functional groups. Thermal stability was measured with a STA 409 PC thermal analyzer (NETZSCH, Germany) at a heating rate of 10°/min in nitrogen atmosphere.

2.5. Adsorption and desorption of Pb^{2+}

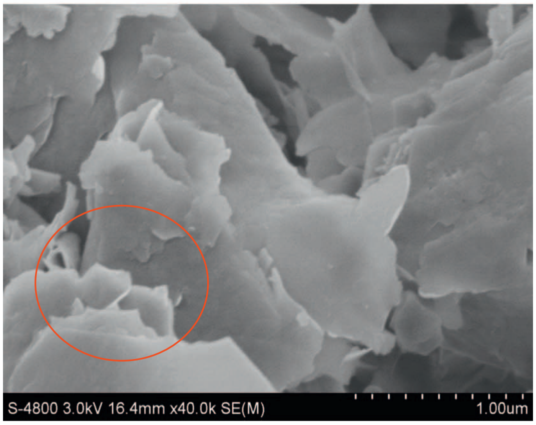
In adsorption kinetic experiments, $Pb(NO_3)_2$ solution (0.2 g/L Pb^{2+}) were adsorbed with the RecCPN adsorbents (0.5 g/L) at pH = 5 in glass bottles. The glass bottles were shaken at 100 rpm in a slow-moving platform shaker. Pb^{2+} concentrations were tested at the different times (0 – 2 h) with an atomic adsorption spectrometer (Thermo Scientific iCE 3000). For adsorption isotherm study, the initial Pb^{2+} concentrations varied from 0.05 to 0.4 g/L with the adsorbent RecCPN (0.5 g/L). The temperatures were respectively kept at 25, 30 or 35 °C, and the adsorption was operated on a rotary shaker at 100 rpm for 2 h to reach the adsorption equilibrium. An atomic adsorption spectrometer was used to test the Pb^{2+} concentrations, which were used to calculate the equilibrium adsorbed amounts of Pb^{2+} for the solutions with the different Pb^{2+} initial concentrations.



(a) Rec



(b) RecCN



(C) RecCP2N

Fig. 1. SEM images of Rec (a), RecCN (b) and RecCP2N (c).

In the experiments of Pb^{2+} readsorption, 5 mg RecCP2N was added to 10 mL of Pb^{2+} solution (0.2 g/L). After 2 h in the shaker at 100 rpm, Pb^{2+} concentrations were determined with an atomic adsorption spectrometer. The separated RecCP2N was dried, and immersed in 10 mL of ethylenediaminetetraacetic acid disodium salt (EDTA) solution (0.1 mol/L) for 2 h to remove Pb^{2+} from RecCP2N. The obtained RecCP2N was used for another Pb^{2+} adsorption.

Competitive adsorption experiments of RecCN and RecCP2N were conducted as the initial $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Ni(NO_3)_2$ and