



Research article

Heterocoagulated clay-derived adsorbents for phosphate decontamination from aqueous solution



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ABSTRACT

A series of nanocomposite adsorbents were prepared by heterocoagulation of negatively charged delaminated montmorillonite (M_t) and positively charged synthetic layered double hydroxide (LDH) colloids with different LDH loading amounts. The mineralogy and physicochemical properties of the resulting nanocomposites were characterized. Their potential applications for phosphate (P) removal from aqueous solution, as a function of P concentration (2.5–200 mg/L), contact time (1 min–48 h) and pH (3–10), were evaluated by using batch adsorption modes. It was found that the adsorption data could be well described by both Freundlich and Langmuir isotherm models. The maximum adsorption capacity of three different LDH heterocoagulated montmorillonites (LDH- M_{ts}) for P removal was found to increase with LDH loadings, reaching 12.6, 16.2 and 23.3 mg/g respectively; Adsorption kinetic data revealed that 90% of adsorption onto LDH- M_{ts} was completed within 1 h (h) and the adsorption process could be well described by the pseudo-second-order model. These results demonstrated that heterocoagulation of M_t and LDH could preserve the adsorption capacity of LDH for P and enhance the stability of both clay minerals, and LDH- M_{ts} could be effectively used as a potential promising filtration medium for P removal.

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1. Introduction

Phosphorus mainly occurs as phosphate (P) with low concentrations in aqua-systems (Das et al., 2006). Although it is an essential nutrient for growth of micro-organisms in the aquatic environment, excess phosphorus discharged from wastewater or agricultural applications to lakes, lagoons, rivers and seas will result in eutrophication of the water bodies (Gan et al., 2009). Eutrophication in lake water has become one of the most important factors impeding sustainable economic development in China and some other countries (Le et al., 2010). To further prevent eutrophication, the U.S. EPA set stringent limits for total phosphorus in natural waters, i.e., 0.1 mg/L for rivers and 0.05 mg/L for rivers draining into lakes (Kumar et al., 2014). Many techniques have been proposed for

phosphate removal from wastewater, and adsorption has emerged as one of the most promising methods in preventing eutrophication due to its high efficiency, easy handling, different available adsorbents and low cost (Dwivedi et al., 2008).

Though numerous previous studies have been focused on development of advanced adsorbents, those adsorbents are often too expensive to be used in practice. There have been considerable research efforts in developing modified adsorbents for specific applications based on natural clay minerals, such as bentonite, due to their abundance, high specific surface area and charged layer structure. Al-Asheh et al. (2003) treated bentonite with sodium chloride solution and surfactants or pillaring reagents to adsorb phenol. Eren (2009) modified bentonite with manganese oxide to remove large organic cation from aqueous solutions. Borgnino et al. (2009) prepared Fe-montmorillonites for phosphate adsorption. Some bentonites were heated or acid-treated to activate the adsorption sites to remove persistent pollutant chlorobenzene (Sennour et al., 2009), Bezanyl Red and Nylomine Green (Benguella and Yacouta-Nour, 2009). Various pillared bentonites have been used for the adsorption of heavy metals (Yan et al., 2008),

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phosphate (Kasama et al., 2004; Yan et al., 2010), fluoride (Bia et al., 2012) and hydrogen sulfide (Danh et al., 2005). Suitable surfactants were loaded on bentonite surfaces to enhance their hydrophobic properties towards organic materials, such as phenol (Zhu and Zhu, 2007), naphthalene and phenanthrene (Ma and Zhu, 2006). Many other techniques were also applied to enhance adsorption capacity for various pollutants, such as grafting surfactants onto aluminum/chromium-intercalated bentonite (Bouberka et al., 2009). However, the common negatively charged clay minerals such as bentonites are effective in cation removal, but not effective for phosphate anions (Eren, 2009).

Synthetic layered double hydroxides (LDHs) are positively charged and could be used to adsorb anionic species (Chitrakar et al., 2011). However, due to small particle size and swelling colloidal properties of LDHs, it is difficult to apply them as flow-through filtration media; therefore, it is desired to enhance the stability of the LDHs in the water treatment process without losing the adsorption capacity for phosphate. Many different solid materials have been reported to be used as stabilizers or substrates for developing adsorbents, such as iron oxides, silica, alumina, calcium carbonate, barium sulfate, carbon, polystyrene, colloidal metals and clay minerals (Abend et al., 1998). Clay minerals should be excellent solid stabilizers because they are available in large amounts and great diversity. The materials most suitable for applications are the various layered montmorillonite. Montmorillonite is a kind of cationic clay, and it is also the characteristic mineral composition of bentonite, while LDH is a sort of anionic clay. This means that the LDH can function as the cation and the montmorillonite as the anion. Therefore, the objective of this study was to develop low-cost, LDHs-derived nanocomposite adsorbents by heterocoagulation of montmorillonite and LDHs for remediating P contamination.

2. Materials and methods

2.1. Preparation of the LDH-heterocoagulated montmorillonites (LDH-M_{ts})

The Mg/Al layered double hydroxide (LDH) was prepared by adding an aqueous solution of NaOH (2.0 M) dropwise to a mixed aqueous solution of MgCl₂ and AlCl₃ (total metal concentration of 1.0 M with a Mg²⁺/Al³⁺ molar ratio of 3.0) into a large beaker. The temperature of the reaction mixture was maintained at 25 (±1) °C during the titration. The mixture was stirred for 3 h, transferred to plastic bottles, and aged in an oven at 65 °C for 4 days. Then the suspension was centrifuged and the precipitate was washed extensively using deionized water until free of chloride (AgNO₃ test). The product was dried at 65 °C, ground and stored in polyethylene bottles before use (Zhao and Nagy, 2004; Gan et al., 2011). The divalent metal and trivalent metal compositions of parent LDH, as analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), indicated that the Mg:Al molar ratio of the synthesized Mg/Al LDH was found to be 2.78, which was in accordance with the analysis of its energy dispersive spectroscopy (EDS) image (Fig. 1) (Gan et al., 2011).

The natural montmorillonite clay mined from the Tuokexun County (Xinjiang province, China) was manually ground and passed through a 0.15 mm sieve. The <2 μm fraction was separated according to Stokes' Law. The pH of extracted montmorillonite was about 7.10, and its chemical analysis was (W_t%): SiO₂, 58.73; Al₂O₃, 16.51; Fe₂O₃, 5.16; CaO, 1.16; MgO, 2.86; Na₂O, 1.22; K₂O, 1.65; P₂O₅, 0.04; TiO₂, 0.49; LOI, 14.12. Ten grams of the extracted montmorillonite (M_t) were dispersed into 500 ml of water, then 1.5, 3.0 and 6.0 g LDH was added to a certain amount of distilled water to achieve 10% LDH solution, respectively. After 24 h of stirring, three

LDH solutions were added dropwise to the clay suspension and stirred for another 24 h (mass ratios of 6.7, 3.3 and 1.7). To remove the excess LDH, this suspension was centrifuged and the precipitate was washed using deionized water for 5 times. The products were dried at 65 °C, ground and stored in polyethylene bottles before use, which were labeled as LDH-M_{t1}, LDH-M_{t2} and LDH-M_{t3}, and the suspension pH were tested to be around 8.1. As seen from EDS images (Fig. 1a), LDH-coating dramatically changed the Mg:Al molar ratio, which was 0.61, 0.90 and 1.26 for LDH-M_{t1}, LDH-M_{t2} and LDH-M_{t3}, respectively.

All chemical reagents used were of analytical-reagent grade and obtained from Ronghua Co. (Nanjing, China).

2.2. Batch adsorption experiments

The maximum phosphate adsorption capacity was determined using a batch equilibrium technique as described below. Initially, a stock solution of 1000 mg/L in P was prepared by dissolving a certain amount of chemically pure KH₂PO₄ in distilled water. Eight levels of phosphate concentrations, ranging from 2.5 to 200 mg/L (2.5, 5, 10, 20, 50, 100, 150, 200 mg/L) for M_t, LDH and LDH-M_{ts} were tested. 0.1 g of extracted natural montmorillonite, LDH and LDH-M_{ts} were loaded in 100 ml conical flasks containing 25 ml of different P solution. The flasks were continuously shaken on a sway gyratory shaker (HZ-9310 K, China) at 200 rpm for 24 h at 25 °C.

Phosphate adsorption kinetics of LDH-M_{ts} was evaluated at room temperature (25 °C) and at original pH value. The initial phosphate concentration was 50 mg P/L with the adsorbent quantity of 0.1 g, and the solution volume was maintained at 25 ml. Reaction solutions were sampled at intervals between 0 and 48 h during adsorption with different intervals at 25 °C.

The effect of different pH levels (ranging from 3 to 10) on phosphate removal by LDH-M_{ts} was also investigated. The tests were carried out at 25 °C for 24 h, by using 25 ml of 50 mg/L phosphate solution and 0.1 g adsorbent.

After phosphate adsorption, the solution was analyzed for P. The quantity of adsorbed phosphate was calculated from the decrease of the phosphate concentration in the solution.

2.3. Adsorbents characterization

X-ray diffraction (XRD) patterns of the prepared samples were acquired with a D/MAX2200 X-ray diffractometer using CuKα radiation (40 kV, 40 mA) and a Ni filter. All XRD patterns were obtained from 2.0° to 50.0° with a scan speed of 4.0°/min. The quantitative analysis by XRD used internal standards by comparing reflection from standard substance and from components. A scanning electron microscope Hitachi S-3400N was used for scanning electron microscopy (SEM) and EDS analysis. Chemical analyses of the adsorbents were determined by the LiBO₂-ICP-AES method, using an induced coupled plasma atomic emission spectrophotometer (Thermo IRIS Advantage). The analysis of phosphate (as phosphorous) was done by the molybdenum-blue ascorbic acid method with a UV-Vis spectrophotometer (UV/VIS 721 model).

3. Results

3.1. Mineralogy of LDH-heterocoagulated montmorillonites

The XRD patterns of parent LDH, and the LDH-heterocoagulated products were shown in Fig. 2. According to the XRD peak intensities, the natural sample contained montmorillonite with a *d*₁₁₀ value of 15.3 Å and moderate reflections of 10.1, 9.02 and 2.57 Å. The peaks originating from quartz were observed with the *d*₁₀₀ and *d*₁₀₁ values of 4.25 Å and 3.34 Å, respectively. A trace amount of kaolinite

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