



Research paper

Kinetics, isotherms and multiple mechanisms of the removal for phosphate by Cl-hydrocalumite

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ABSTRACT

A laboratory study was conducted to evaluate phosphate removal from aqueous solutions by a CaAl–Cl layered double hydroxide (Cl-hydrocalumite). Cl-hydrocalumite was prepared by co-precipitation and was characterized by scanning electron microscopy equipped with energy-dispersive spectrometer (SEM-EDS), powder X-ray diffraction (PXRD), and Fourier transform infrared (FTIR). SEM demonstrated that a crystalline structure was synthesized and PXRD or FTIR spectra revealed that the structure was Cl-hydrocalumite. Adsorption experiments were performed as a function of contact time and initial phosphate concentration. Phosphate adsorption reached equilibrium within 10 h, followed by a pseudo-second-order kinetic model with $R^2 = 0.999$. The experimental data followed the Langmuir and Fedlich–Peterson isotherm models, and showed a maximum adsorption capacity of $\sim 182.5 \text{ mg g}^{-1}$. The Freundlich constant $n = 3.18 > 1$, represented a favorable phosphate adsorption process. SEM-EDS, PXRD, and FTIR analyses of P-hydrocalumite (after adsorption) were used to elucidate adsorption mechanisms. EDS results indicated that chloride was topotactic, exchanged by phosphate to generate P-hydrocalumite, and partial Cl-hydrocalumite was dissolved. The PXRD and FTIR spectra indicate that P-hydrocalumite was a mixture with a new precipitate, brushite. Phosphate adsorption by Cl-hydrocalumite was topotactic anion exchange combined with dissolution–reprecipitation. Cl-hydrocalumite was a cost-effective and excellent phosphate adsorbent.

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1. Introduction

As one of the 17 elements needed by plants, phosphorus (P) is a vital component of many macromolecules in plants, which can't be substituted by any other element (Li et al., 2011). Increasing global population and a rising demand for food and industrial products has led to global phosphates being depleted progressively. Gilbert predicts that global phosphate rock deposits will be depleted by 2050 (Gilbert, 2009). However, during agricultural fertilization and industrial production, phosphates (e.g., organic, inorganic, oligo-, and polyphosphates (Ashkuzzaman and Jiang, 2014)) in abundant wastewater are discharged into environmental water bodies (e.g. lakes, lagoons, rivers, and seas (Das et al., 2006)). Wastewater discharged without treatment has led to water pollution or severe aquatic ecosystem problems (Zhou et al., 2011), such as eutrophication (Yang et al., 2014), and also significant wastage of phosphorus resources.

In recent decades, the removal and recovery of phosphorus from wastewater has been a topic of concern and a research field of significant interest. Municipal wastewater treatment plants possess some

techniques to remove phosphorus, including traditional chemical precipitation, biological treatment, adsorption, and crystallization (Ashkuzzaman and Jiang, 2014). Adsorption is more suitable and compatible with satisfying industrial requirements since it displays many advantages such as easy operation, fast treatment, reduced secondary sludge, and is recoverable and cost-effective (Xu et al., 2010; Theiss et al., 2014). Various types of materials have been used as phosphate adsorbents, such as hybrid anion exchangers, polymeric hydrogels (Mayer et al., 2013), red mud, blast-furnace slag, activated alumina, layered double hydroxides (LDHs), goethite, and manganese nodule leached residue (Das et al., 2006; Yang et al., 2014). Among them, layered double hydroxides have received attention because of their excellent properties, such as high anionic adsorption capacity, adsorbent recyclability, and environmental friendliness (Woo et al., 2011; Zhou et al., 2011).

LDHs, namely hydrotalcite-like compounds, can be described as cadmium iodide-type layered hydroxides (e.g. brucite, $\text{Mg}(\text{OH})_2$) (Jiang and Ashkuzzaman, 2012), and are a kind of nanosized structural anionic clay. Their general material formula can be written as $[\text{M}_1^{2+}{}_x\text{M}_2^{3+}(\text{OH})_2]^{x+}(\text{A}_x/n)^- \cdot \text{H}_2\text{O}$, where M^{2+} and M^{3+} denote di- and trivalent cations, respectively. When $\text{M}^{2+}/\text{M}^{3+}$ represents $\text{Ca}^{2+}/\text{Al}^{3+}$, the material is hydrocalumite-like LDH, which is termed

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Friedel's salt (Vieille et al., 2003). A^{n-} represents an interlayer anion of valence n , such as NO_3^- , Cl^- , and CO_3^{2-} . x is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$, and typically ranges from 0.2 to 0.4 to form a pure LDH phase (Cai et al., 2012; Ashekuzzaman and Jiang, 2014). The layer of LDHs was positively charged by isomorphous substitution of trivalent for divalent cations (Kuzawa et al., 2006). Because of its nanostructure (huge surface area) and positively charged layers, LDHs generally have a good anion exchange capacity and selectively adsorb various anions (greater affinity to multi- than monovalent cations) (Tezuka et al., 2004; Goh et al., 2008; Baliarsingh et al., 2013).

Many studies have been conducted to synthesize various hydroxylated-like LDHs by different methods and using different materials for phosphate removal. Goh et al. stated that calcined LDHs ($34\text{--}82\text{ mg g}^{-1}$) show a higher phosphate adsorption capacity than uncalcined LDHs ($29\text{--}47\text{ mg g}^{-1}$) (Goh et al., 2008). Kuzawa et al. prepared granular MgAl-Cl LDH composites with poly-acrylate binder, and found that the maximum phosphate adsorption capacity corresponds to the MgAl-Cl LDH content (Kuzawa et al., 2006). Limited reports exist on phosphate removal by hydrocalumite-like LDHs. Zhou et al. applied the PHREEQC program to simulate the behavior of phosphate uptake by hydrocalumite, and believe that it occurred by pH-dependent dissolution–reprecipitation, the program is a low-temperature aqueous geochemical calculation computer program which can be applied to model precipitation-dissolution equilibrium (Zhou et al., 2012). We synthesized hydrocalumite-like LHD by co-precipitation, characterized the product by powder X-ray diffraction (PXRD), scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS), and Fourier transform infrared spectroscopy (FTIR) to obtain direct proof for and to determine the mechanism of phosphate removal by hydrocalumite. We also studied the kinetics and isotherms of phosphate uptake to understand this adsorption behavior further. Our results provide evidence to confirm the mechanism of phosphate removal by hydrocalumite-like LDHs.

2. Materials and methods

2.1. Preparation of Cl-hydrocalumite

The reagents used in this study were of analytical grade and purchased from Nanjing Chemical Reagent Co. Ltd. (Nanjing, China). Solutions were prepared using deionized water ($>5\text{ M}\Omega$) as solvent. Hydrocalumite-like Cl-LDH (abbreviated as Cl-hydrocalumite) was synthesized by traditional co-precipitation (Lv et al., 2007). This method contains two main processes: (1) high-speed stirring for nucleation and (2) a separate drying and aging process. $\text{Ca}(\text{OH})_2$ powder (22.0 g) and NaAlO_2 solution (1 M, 75.0 ml) were added simultaneously to a 1 l beaker, which already contained 600 ml 10 wt% HCl. The mixture pH was adjusted to 6–7 by drop-wise addition of 1 M HCl or 1 M NaOH. The mixture was stirred at 150 rpm for 1 h at room temperature, collected by filtration and rinsed thoroughly with deionized water. The final precipitate was dried in an oven (Shanghai CIMO Medical Instrument Manufacturing Co. Ltd., Shanghai, China) at $60\text{ }^\circ\text{C}$ for further study. The metal composition of the sample was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS Advantage, Thermo Jarrell Ash/Baird, Massachusetts, USA). All of the pH values were monitored with a METTLER TOLEDO pH meter (Model SG78, METTLER TOLEDO, Zurich, Switzerland), and before each measurement the meter was calibrated.

2.2. Physical characterization

To study the structural patterns of the synthesized hydrocalumite, powder X-ray diffraction (PXRD) analysis was performed on a Phillips X' PERT X-ray Diffractometer, using $\text{Cu K}\alpha$ radiation at a scanning speed of 2° min^{-1} (2θ , $5\text{--}90^\circ$). Powder data files (ICDD-JCPDS) were

applied to analyze the patterns. The morphology of the hydrocalumite samples was examined by Hitachi S4800 field emission SEM equipped with an EDS. The FTIR spectra were collected on a Nicolet 5700 FTIR spectrometer using a transmission model in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$.

2.3. Removal experiments

From a preliminary study, the sorption of phosphate by Cl-hydrocalumite reached equilibrium at $\sim 10\text{ h}$, and later sorption trials were shaken for 24 h to ensure the system reached equilibrium (except for the study of adsorption kinetics). The pH of all synthetic phosphate solutions was between 4 and 7. All adsorption experiments were conducted in screw-top centrifuge tubes (Corning, NY, USA) in a thermostatic oscillator (150 rpm) (ZQTY-70F, Shanghai Zhichu Instrument Co., Ltd., China) at room temperature. All runs were conducted in triplicate.

To investigate the kinetics of phosphate adsorption by Cl-hydrocalumite, 0.10 g Cl-hydrocalumite was added to 40 ml NaH_2PO_4 (500 mg P l^{-1}) solution. After appropriate shaking intervals, the suspension was withdrawn and filtered immediately using a $0.22\text{ }\mu\text{m}$ membrane (XingYa Materials Plant, Shanghai, China). The phosphate concentration in the filtrate was determined by ICP-AES.

The adsorption isotherm was studied by preparing solutions of different concentrations (from 10 to 1800 mg P l^{-1}) using NaH_2PO_4 , and 0.08 g Cl-hydrocalumite was added to 40 ml phosphate solutions.

3. Results and discussion

3.1. Adsorption kinetics

An experiment on the effect of contact time was carried out to study the adsorption kinetics of phosphate adsorption. The experimental results are presented in Fig. 1. The adsorption process contained two stages: (a) a fast adsorption stage with almost linear increase in adsorption percentage in 1.5 h, which reached 52.7%, and (b) a slow adsorption stage, between 1.5 and 10 h, during which the P uptake increased slightly from 52.7% to 57.3%, before reaching equilibrium.

The process can be described as a rapid phosphate adsorption step followed by a slower step controlled by the rate of the reaction between Cl-hydrocalumite and phosphate, and agrees with other reports (Cai et al., 2012; Novillo et al., 2014). In general, three common mechanisms were involved during oxyanion adsorption by LDHs, i.e., (1) external mass transfer such as boundary layer/film diffusion between the external surface of the sorbent particles and the surrounding fluid phase, (2) intra-particle transport within the particle, and (3) chemisorption

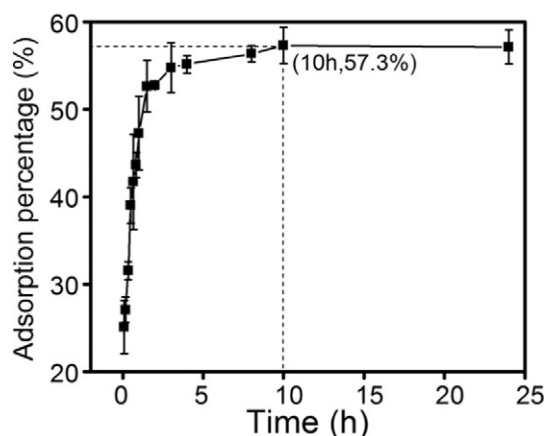


Fig. 1. Variation of phosphorus adsorption by Cl-hydrocalumite as a function of the time.

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