Adsorption of phosphate by acid-modified fly ash and palygorskite in aqueous solution: Experimental and modeling

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ABSTRACT

In this study, a class F fly ash and palygorskite have been acid-modified and then evaluated for the adsorption of phosphate in aqueous solution via bench-scale batch experiments. XRD, XRF, SEM, and FTIR were employed to characterize the acid-modified fly ash (MFA) and palygorskite (MPal). Both MFA and MPal show enhanced phosphate adsorption after the modification treatment. The effects of pH, adsorbent dosage, and co-ions on phosphate adsorption, as well as adsorption thermodynamics and kinetics, and leaching features of spent (used) adsorbents were also investigated. The isotherms data fit well with the Langmuir model rather than the Freundlich model, giving maximum capacities (298 K) of 13.3 mg P g^{-1} for MFA and 10.5 mg P g^{-1} for MPal, respectively. Surface complexation modeling of P adsorption data with the nonelectrostatic generalized composite (GC) approach indicates that phosphate were directly bound to the metal centers by ligand exchange to form two monodentate complexes, $\equiv SHPO_4^-$ and $\equiv SPO_4^{2-}$. The GC model appears to be an easy and efficient tool to provide an insight into the mechanism of phosphate adsorption on complex adsorbents with limited model parameters. Leaching test results suggest that the spent adsorbents can be safely disposed or further reused.

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1. Introduction

Phosphorus (P) is an essential nutrient to the growth of aquatic algal and other biological organisms; however, the excessive presence of phosphate in natural water bodies, especially lakes or reservoirs, will lead to algal blooms and eventually results in degeneration of water quality. This process is well known as eutrophication (Correll, 1998). Eutrophication of the Taihu Lake (Jiangsu, China) in the summer of 2007 caused a serious water crisis to both domestic and industrial users. Removal of phosphate, using either chemical or biological technologies, from such water bodies and inflows can therefore be effective to control the eutrophication of the lakes. Phosphate can be removed from wastewater by adsorption, ion-exchange, precipitation, biological uptake, etc. (Mayer et al., 2013). Of these approaches of phosphate removal, adsorption has attracted more attention due to its simplicity, stability, and operability (Agyei et al., 2000; Das et al., 2006; Yan et al., 2007; Haghseresht et al., 2009; Zamparas et al., 2012). The adsorption of phosphate by commercial adsorbents, industrial by-products, and clay minerals has been practiced for decades. Industrial by-products (e.g., fly ash) and natural clays (e.g., palygorskite, bentonite) are getting more attractive in phosphate removal other than commercial adsorbents due to their lower cost, abundance, and excellent adsorption capabilities (Ye et al., 2006; Yan et al., 2007; Gan et al., 2009; Haghseresht et al., 2009; Zamparas et al., 2012). In fact, there are a variety of fly ash sources (e.g., coal-fired power plants) as well as clay mines (e.g., palygorskite mines) around the Taihu lake. It would be promising to solve the eutrophication problem of the Taihu lake if the abundant and cheap fly ash and/or palygorskite can be utilized as adsorbents for phosphorous removal from municipal sewages that used to be discharged into the lake without any treatments.

Fly ash is a by-product derived from the combustion of pulverized coal in power plants. The utilization of fly ash for phosphate removal from wastewaters has been studied extensively recently, and the results have indicated that fly ash is an excellent alternative adsorbent to commercial adsorbents in phosphate adsorption (Ugurlu and Salman, 1998; Agyei et al., 2000, 2002; Grubb et al., 2000; Chen et al., 2007; Lu et al., 2009; Xu et al., 2010). It is reported that most of dissolved phosphate can be efficiently precipitated by the high concentration of calcium in class C fly ash (i.e., one type of fly ash generally contains >20% CaO) (Ugurlu and Salman, 1998; Lu et al., 2009). For class F fly ash (i.e., one type of fly ash contains <7% CaO), metal oxides in fly ash, such as Al_2O_3, Fe_2O_3, etc., can also uptake phosphate efficiently (Grubb et al., 2000; Chen et al., 2007). The phosphate adsorption capacity of class C fly ash is generally greater than that of class F fly ash due to the additional contribution from precipitation by the high content of calcium in Class C fly ash besides the adsorption of phosphate by metal oxides in both types of fly ashes (Agyei

et al., 2000; Grubb et al., 2000; Chen et al., 2007; Yan et al., 2007). On the other hand, palygorskite (Pal, $(Mg,Al)_5(Si,Al)_8O_{20}(OH)_2 \cdot 8H_2O$) is a naturally occurring layered aluminum silicate mineral, which was widely used in catalyst, catalyst supports (Zhang et al., 2010, 2014; Pushpaletha and Lalithambika, 2011), and adsorbents (Ye et al., 2006; Gan et al., 2009). Previous studies have confirmed that phosphate can be effectively removed by both natural and modified palygorskites (Ye et al., 2006; Gan et al., 2009).

To obtain a higher adsorption capacity, some surface modifications (e.g., introducing or incorporating new groups, thermal treatment, acid activation, etc.) to these adsorbents are required. Haghseresht et al. (2009) found that incorporating lanthanum into bentonite can improve its adsorption capacity for phosphate in aqueous solution. Similarly, a recent study by Zamparas et al. (2012) also showed that iron-modified bentonite can uptake more phosphate than unmodified bentonite. Indeed, the other two typical modification methods, i.e., thermal treatment and acid activation have long been used to produce sorbents for certain practical applications (Bergaya et al., 2006). It is suggested that thermal treatment of palygorskite can increase its adsorption capacity for phosphate (Gan et al., 2009). Ye et al. (2006) also investigated the effects of either thermal treatment or acid activation of palygorskite on phosphate adsorption, and suggested that both modification approaches can improve phosphate adsorption efficiently. Research by Li et al. (2006b) using class F fly ashes (FA) as adsorbent for phosphate had elucidated that both thermal treatment and acid activation can significantly enhance its adsorption capacity. It was also reported that both class F and class C fly ashes modified with sulfuric acid possess a higher phosphate adsorption capacity as compared to the original fly ashes due to the dissolution of the amorphous siliceous spherical particulates that embedded active components for phosphorous adsorption (Liang et al., 2010; Xu et al., 2010).

To gain an insight into the adsorption mechanism of phosphate onto mono-component adsorbent, surface complexation modeling is generally employed to quantitatively description of phosphate adsorption data (Goldberg and Sposito, 1985; Bleam et al., 1991; Nilsson et al., 1996; He et al., 1997; Gao and Mucci, 2001; Rahnemaie et al., 2007). For multi-component or complex adsorbents, however, it still remains a great challenge to use surface complexation modeling to explore the adsorption mechanism due to the complication, even though only a few attempts using constant capacitance model (CCM) (Grubb et al., 2000) and chemical equilibrium model (Johansson and Gustafsson, 2000) has been made. To date, the only successful example of modeling the adsorption data of complex adsorbents is the generalized composite (GC) modeling approach, which was developed by Davis et al. (1998), and can successfully describe and predict the adsorption behaviors of many radionuclide and rare earth ions onto soils (Davis et al., 2004; Tertre et al., 2008). However, GC modeling approach had not been used to fit and predict phosphate adsorption on complex adsorbents yet. To the best of our knowledge, this is the first work that shows how to use the powerful GC modeling approach to describe P adsorption over complex adsorbents, gaining insights into the mechanism of phosphate adsorption.

The objective of this study was twofold: first, to examine the feasibility of using acid-modified fly ash and palygorskite (termed as MFA and MPal) as adsorbents for phosphate uptake in aqueous solution via batch experiments, and second, to gain an insight into the adsorption mechanism of both acid-modified adsorbents via the GC surface complexation modeling. The influences of pH, co-ions, and adsorbent dosage on phosphate adsorption have been studied. Equilibrium and kinetics studies were also performed and fitted with related isotherm models (i.e., Langmuir and Freundlich models) and a kinetic model (i.e., the pseudo second-order rate model). Leaching tests were also conducted to evaluate the safety of disposal or further reuse of the spent (used) adsorbents.

2. Materials and methods

2.1. Materials

Class F fly ash (FA) was obtained from the electrostatic precipitator (ESP) ash-hopper III of No. 4 pulverized coal (lignite bituminous coal) boiler at Huaneng Changxing power plant (located in the southwest lakeshore of the Taihu lake), while the palygorskite (Pal) was originated from Xuyi County (Jiangsu, China). The chemical components of both FA and Pal were measured by X-ray fluorescence spectroscopy (XRF), and the results are listed in Table 1. All other chemicals (analytic reagent (A.R.) grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used as received. Milli-Q ultrapure water (18.2 M$\Omega \cdot$cm resistivity at 298 K) was used in all experiments.

2.2. Modification procedure

Three types of acid solution (Ye et al., 2006; Liang et al., 2010), including H_2SO_4 (2 mol L^{-1}), HCl (2 mol L^{-1}), and H_2SO_4–HCl mixture (1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} HCl), were used to etch the original materials, i.e., fly ash and palygorskite. Typically, 20 g of FA or Pal was ground to pass through a 160 mesh-sized sieve (size <94 μm), followed by drying in 393 K (120 °C) oven and then well mixing with 100 mL of etching solution (e.g., 1 mol L^{-1} H_2SO_4 + 1 mol L^{-1} HCl) for 30 min under ultrasonication. The mixtures were then filtered and washed with excess water to provide salt-free sediments, followed by drying in oven (393 K), cooling to ambient temperature, and regrinding. Finally, the modified FA and Pal (termed as MFA and MPal, respectively) were resieved to pass through a 160 mesh-sized sieve prior to collecting and storing for further tests.

2.3. Characterization

X-ray diffraction (XRD) measurement was performed on an ARL X'TRA diffractometer (ARL, Switzerland) at a voltage of 40 kV and a current of 30 mA with Cu-Kα radiation. XRF data were collected on an ARL–9800 spectrometer following the fused–disc method (Li et al., 2006a). Scanning electron microscopy (SEM) was conducted on an S-3400 N microscope (Hitachi, Japan) with an accelerating voltage of 20 kV. Fourier transform infrared (FTIR) spectra were recorded on a NIKOLET Nexus 870 spectrometer (Thermo Fisher, USA) following the KBr–pressed–disc method (Li, 2013).

2.4. Phosphate adsorption tests

Phosphorous stock solutions (1000 mg L^{-1}) were prepared using A.R. grade K_2HPO_4. The effect of adsorbent dosage on phosphate adsorption was evaluated first, and the results (see Fig. S1 in the *supplementary data*) indicated that a dosage of 2 g L^{-1} of adsorbents is the optimum value in consideration of efficiency and costing. The pH effect experiments were performed to determine the adsorption envelope, which is the percentage of phosphorous adsorbed as a function of the solution pH. Dispersions containing 10 mg P L^{-1} (0.3226 mM) phosphate and 2 g L^{-1} adsorbents were adjusted to a desired pH in the range of 3–12 by using 0.1 M NaOH and HCl solution. After shaking on a rotary shaker at 200 rpm for at least 24 h to obtain equilibrium states, the suspensions were filtered with 0.45 μm cellulose membrane for P concentration measurement. Typical ions including F^-, SO_4^{2-}, CO_3^{2-}, Zn^{2+}, Cu^{2+}, and Al^{3+} (using NaF, Na_2SO_4, $Na_2CO_3 \cdot H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2$, and $Al(NO_3)_3$ as source salts, respectively) with concentrations of 5–40 mg L^{-1} were also selected to investigate the effect of co-ions on phosphate adsorption with a dosage of 2 g L^{-1} at pH 7.5 ± 0.1.

Adsorption kinetics experiments were carried out by reacting 10 mg P L^{-1} of phosphate with 2 g L^{-1} adsorbents at pH 7.5 ± 0.1. The kinetic data were fitted with the pseudo second-order rate model (Ho and