Comparison study of phosphorus adsorption on different waste solids: Fly ash, red mud and ferric–alum water treatment residues

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ABSTRACT

The adsorption of phosphorus (P) onto three industrial solid wastes (fly ash, red mud and ferric–alum water treatment residual (FAR)) and their modified materials was studied systematically *via* batch experiments. Compared with two natural adsorbents (zeolite and diatomite), three solid wastes possessed a higher adsorption capacity for P because of the higher Fe, Al and Ca contents. After modification (*i.e.*, the fly ash and red mud modified by $FeCl_3$ and FARs modified by HCl), the adsorption capacity increased, especially for the modified red mud, where more Fe bonded P was observed. The P adsorption kinetics can be satisfactorily fitted using the pseudo-second-order model. The Langmuir model can describe well the P adsorption on all of the samples in our study. pH and dissolved organic matter (DOM) are two important factors for P adsorption. Under neutral conditions, the maximum adsorption amount on the modified materials was observed. With the deviation from pH 7, the adsorption amount decreased, which resulted from the change of P species in water and surface charges of the adsorbents. The DOM in water can promote P adsorption, which may be due to the promotion effects of humic-Fe(Al) complexes and the pH buffer function exceeds the depression of competitive adsorption.

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Introduction

Excess phosphorus (P) in a water body can cause eutrophication and significant environmental problems to water resources (Lürling et al., 2014; Paerl et al., 2011). The enhancement of P removal in waste effluents before their discharge into the environment is thus of considerable significance. Presently, various techniques have been successfully applied for P removal, such as physical (*e.g.*, adsorption, and filtration), chemical (*e.g.*, chemical precipitation and ion exchange), and biological (*e.g.*, plant uptake and microbial degradation) techniques. Among these techniques, adsorption is one of the most attractive approaches, with the advantages of operation simplicity, low operation cost and ability to provide effective removal without yielding harmful by-products.

Many types of adsorbents for phosphate removal have been investigated that are mainly divided into two types: industrial solid wastes (Cao et al., 2013; Castaldi et al., 2010; Liu et al., 2007; Wang et al., 2011) (fly ash, red mud, ferric–alum residuals, *etc.*) and natural/synthetic mineral materials (Borggaard et al., 2005; Huang et al., 2009; Wang and Peng, 2010; Xiong and Peng, 2008) (zeolites, diatomite, aluminum

oxides, iron, iron oxides, *etc*.). Every year, the enormous quantity of industrial solid wastes generated from power plants, mineral extraction, and so on contributes to very serious and alarming environmental problems. Some of these solid wastes (such as fly ash, red mud, slag, and Fe/Al residual) have been demonstrated to have a remarkable adsorption capacity for phosphate because these materials are enriched with oxides of aluminum, iron and calcium (Liu et al., 2007; Wang et al., 2011). Therefore, even though some natural/synthetic materials possess good P adsorption capacity (Huang et al., 2009; Liu et al., 2013; Xiong and Peng, 2008), the use of the solid wastes for P adsorption is a more promising suitable way for waste utilization.

The P adsorption capacities of solid wastes depend on both their properties (*e.g.*, particles size, component and surface characteristic) and the experimental conditions (*e.g.*, temperature, initial P concentration and pH) (Özacar, 2003; Wang et al., 2011). Some researchers found that solid wastes modified by simple methods (such as thermal treatment, inorganic salt treatment, and inorganic acid or alkali treatment) showed higher P adsorption capacity. For example, fly ash was modified by NaOH or HCl to change the surface characteristics. The P adsorption capacity was found to decrease in the following order: NaOH-fly ash > fly ash > HCl-fly ash (Pengthamkeerati et al., 2008). In addition, the experimental conditions exhibited an obvious influence on P adsorption. Earlier works demonstrated that pH is the most important factor (Yan et al., 2010). In addition, these earlier works demonstrated that Fe–Al residual has a high P adsorption capacity in the pH range of 3.6 to 5.6 (Wang et al., 2011). Also, natural organic matters in water bodies have an influence on the P adsorption (Lürling et al., 2014). **Q3** Those studies revealed that dissolved organic matter (DOM) can compete with P for the adsorption sites and thus decrease the P adsorption (Lürling et al., 2014; Weng et al., 2012).

The objective of this study was to investigate the P adsorption characteristics on three industrial solid wastes (fly ash, red mud and ferric–alum water treatment residuals (FARs)) and their modified materials. **Q4** Their capacity was also compared to two typical natural materials (*i.e.*, zeolite and diatomite). The effects of pH and DOM on the P adsorption were also elucidated.

1. Materials and methods

1.1. Materials

Samples of fly ash, red mud, and FARs were provided by Beijing Shougang Iron Works, Aluminum Corporation of China Limited Shandong branch, and the 9th Water Supply Plant of Beijing, China, respectively. Zeolite and diatomite were purchased from Sinopharm, China. All of the chemical reagents used were analytically pure.

A total of 5 g of the sample of FARs were placed into HCl solution of 2 mol/L. After being shaken for 12 hr, the mixture was centrifuged to obtain the precipitate. Next, the solution was washed using deionized water many times until the solution was neutral. The sample was then dried at 105°C for 3 hr.

Five-gram samples of fly ash or red mud were placed into 500 mL of deionized water, and then, the pH value was adjusted to 13. Subsequently, a 0.5 mol/L of $FeCl_3$ solution was dropped into the mixture slowly with continual stirring until the solution pH decreased to 5. After precipitating for 24 hr, the residue remaining after centrifuging was dried at 105°C for 3 hr. Next, the residue was grinded and passed through a 100-mesh sieve.

1.2. Methods

1.2.1. Adsorption capacity for phosphorus

All of the adsorptive tests in this work were performed in a shaker at 30 ± 1°C. Two drops of 0.1% chloroform were added to inhibit the bacterial activity.

The characteristics of the adsorption kinetics of P were obtained by mixing 0.20 g samples (red mud, fly ash, zeolite and diatomite) and 25 mL of solution with an initial phosphate ion concentration of 100 mg/L. Because the P adsorption capacity of the other materials was considerably higher, the P solution volume was increased to achieve equilibrium. For FARs, modified FARs (m-FARs), modified fly ash (m-fly ash) and modified red mud (m-red mud), the P solution volume was 100 mL. The samples were collected at different time intervals and at different concentrations.

Three kinetic models were used to analyze the experimental data: pseudo-first-order (Eq. (1)), pseudo-second-order (Eq. (2)), and a double-constant rate equation (Eq. (3)).

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{1}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{2}$$

$$\ln Q_t = a + b \ln t \tag{3}$$

where, Q_e (mg/g) is the P adsorption capacity at equilibrium; Q_t (mg/g) is the P adsorption capacity at time t; k_1 and k_2 (hr^{-1} and kg/(kg·hr)) are the rate constants of Eqs. (1) and (2), respectively; t (hr) is the reaction time; and a and b are the kinetic constants.

To study adsorption equilibrium, adsorption isotherms were obtained as follows. Briefly ash, 0.20 g of each of the samples (red mud, fly ash, zeolite and diatomite) was added in a series of 25 mL solutions with initial phosphate ion concentrations of 0, 30, 60, 100, 120, 150 and 300 mg/L. Because the phosphate adsorption capacity of the other materials was considerably higher, the initial phosphate ion concentration was increased to reach saturation, and then, the maximum adsorption capacity was calculated. For FARs, the initial phosphate ion concentrations were 100, 150, 300, 450, 600, 750 and 1000 mg/L. For the three modified materials, the initial phosphate ion concentrations were 100, 300, 600, 750, 1500 and 3000 mg/L. After achieving equilibrium *via* 48 hr of processing in a shaker, the solutions were centrifuged at 5000 r/min for 20 min, and then, the supernatants were used for phosphate analysis. The phosphate adsorbed on the samples was calculated using the difference between the initial and the equilibrium concentrations.

The results were fitted to Langmuir (Eq. (4)) and Freundlich (Eq. (5)) isotherm models. Where Q_m (mg/g) is the monolayer capacity of the sorbent and K, K_F and n are constants.

$$Q_e = \frac{K Q_m C_e}{1 + K C_e^n} \tag{4}$$