Adsorptive removal of phosphate from aqueous solutions using lead–zinc tailings
Shuncai Wang, Rongzhuo Yuan, Xueyong Yu and Chaojie Mao

ABSTRACT
This study explored the feasibility of utilizing lead–zinc tailings for phosphate removal in laboratory experiments. The adsorption isotherm, kinetics and pH effect were examined in batch experiments. The Freundlich and Langmuir isotherm models were used for data fitting. The adsorption kinetics can be best described by the simple Elovich equation. The phosphate adsorption tends to decrease with the increase of pH, from 0.37 mg P/g at pH 2.05 to 0.12 mg P/g at pH 7.01, and tends to increase from 0.12 mg P/g at pH 7.01 to 0.64 mg P/g at pH 12.52. The actual phosphate removal on the tailings could be a consequence of adsorption and precipitation reactions with Fe, Al and Ca. Due to their low cost, this type of tailings has the potential to be utilized for cost-effective removal of phosphate from wastewater.

Shuncai Wang (corresponding author)
Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, No. 1, Xikang Road, Nanjing 210098, China
E-mail: shuncaiwang@163.com

Rongzhuo Yuan
Xueyong Yu
Chaojie Mao
College of Environment, Hohai University, No. 1, Xikang Road, Nanjing 210098, China

Key words | adsorption, isotherm, lead–zinc tailings, phosphate removal

INTRODUCTION
Phosphorus (P) is an essential, often limiting, nutrient for growth of organisms in most ecosystems. However, excessive supply of phosphorus from wastewater into water bodies, such as lakes, rivers and creeks causes eutrophication, resulting in the bloom of aquatic plants, growth of algae and depletion of dissolved oxygen. The phosphate in wastewater can be removed by physicochemical and biological methods. Chemical precipitation with alum, lime and iron salts is often used for the removal of phosphate from wastewater. However, this method is subject to costs and the problem of sludge handling. Moreover, chemical precipitation is less effective when the concentration of phosphate is at trace level (De-Bashan & Bashan 2003). The biological removal of phosphate from wastewater has been developed since 1950s, but only 10–30% of phosphate can be removed by this technology (Ergun 2004). Nevertheless, increasing attention has been paid to adsorptive removal of phosphate from aqueous solutions (Hano et al. 1997; Dönnert & Salecker 1999). The application of low cost and easily available materials in wastewater treatment has been widely investigated during recent years, such as fly ash (Gray & Schwab 1993; Cheung & Venkitachalam 2000; Ageyi et al. 2002), blast furnace slag (Johansson & Gustafsson 2000; Xue et al. 2009), red mud (Akay et al. 1998; López et al. 1998; Li et al. 2006), alunite (Özacar 2003), aluminum hydroxide (Seiki et al. 2003; Tanada et al. 2003), iron oxide tailings (Zeng et al. 2004), spent alum sludge (Huang & Chiswell 2000; Yang et al. 2006) and aluminum- and iron-rich residues (Codling et al. 2000), etc. The removal mechanism is mainly either adsorption or precipitation. The major advantage of using these wastes or by-products for wastewater treatment is cost effectiveness.

The lead–zinc tailing material to be investigated in this study is an industrial waste derived from a mineral processing industry in China. The tailings contain significant amounts of CaO, MnO, Fe₂O₃, Al₂O₃, which may be effective in removing soluble phosphorus, as it is well recognized that CaO, MnO, Fe₂O₃, Al₂O₃ are the important phosphorus adsorbents (Parfitt et al. 1975; Altundogan & Tumen 2001; Tanada et al. 2003; Zeng et al. 2004; Zhu et al. 2009).

The objective of this work was to study the feasibility of using lead–zinc tailings as an adsorbent for phosphorus removal from wastewater. In doing so, the adsorption characteristics of this tailings material for phosphate removal from aqueous solutions were evaluated in small-scale experiments. The adsorption isotherms, kinetics and pH effect were evaluated in batch jar tests by using orthophosphate solutions. The contents of phosphate adsorbed...
on the lead-zinc tailings were tested with a scanning electron microscope and X-ray fluorescence spectrometer. Such work could contribute to understanding the phosphate removal process using lead-zinc tailings.

MATERIAL AND METHODS

Materials

The lead-zinc flotation tailings sample used in the present experiments were obtained from Nanjing lead-zinc flotation plant in China. These samples were dark brown fine-grained solids, which were produced by drying the tailings slurry at 80 °C. The percentage of oxides of the dry tailings is shown in Table 1. The particle size distribution curve of the lead-zinc tailings is shown in Figure 1. The average particle size was measured by sieving. The release of several heavy metals from the raw tailings at pH 3.0 was measured in a prior study. It was found that the release of those heavy metals from the tailings was negligible.

The phosphate (PO$_4^{3-}$) stock solution containing 100 mg P/L was prepared by dissolving potassium dihydrogen orthophosphate (KH$_2$PO$_4$) powders (analytical reagent grade) in distilled water. Phosphate working solutions in different concentrations were prepared by diluting the PO$_4^{3-}$ stock solution with distilled water. The pH value of the PO$_4^{3-}$ working solution was adjusted to 6.7–6.8 with diluted HCl and NaOH before adsorption experiments. This solution was used for batch sorption tests.

General batch adsorption procedure

For determination of phosphate adsorption, 1,500 mg of the tailings was loaded in a 150 mL conical flask, and 100 mL of PO$_4^{3-}$ solution containing 10 mg/L of P was then added. The flask was capped and placed on an orbital shaker at room temperature (20–25 °C) and 180 rpm for 2 h to ensure approximate equilibrium. At the end of the 2 h period, the suspension was filtered through a 0.45-µm membrane filter and then analyzed for PO$_4^{3-}$. This procedure was used in all batch adsorption experiments except for conditional tests. The quantity of adsorbed phosphate (adsorption capacity) was calculated from the decrease of the phosphate concentration in solutions. The duplicate experiments demonstrated the high repeatability of this adsorption method.

Studies of adsorption isotherm and pH effect

Phosphate adsorption isotherm studies were carried out with different initial concentrations of phosphate and a fixed concentration of the tailing material at room temperature. Seven levels of initial phosphate concentrations (5, 10, 20, 30, 40 and 50 mg P/L) were used. The pH was maintained at a defined value (6.6–6.8). The isotherm data on P adsorption were fitted to two two-parameter equations (Freundlich and Langmuir). Using a similar procedure, the effect of pH on phosphate adsorption was examined in a series of experiments that used the same initial phosphate concentration (10 mg P/L) while maintaining pH at different values between 2.05 and 12.52.
Adsorption kinetic measurements

Phosphate adsorption kinetics was evaluated at three temperatures (20, 30 and 40°C) and an initial phosphate concentration of 10 mg P/L. Before the start of each kinetic experiment, approximately 1,500 mg of the tailings powder was loaded in a 150 mL conical flask. Then 100 mL of phosphate solution (10 mg P/L) was added into the flask. The flask was covered and immediately placed in a water bath oscillator. The pH was controlled at a defined value (6.6–6.8). Several millilitres of reaction solution was sampled with an air displacement pipettor at various time intervals between 0 and 2 h of adsorption. The sampled solution was immediately filtered through a 0.45 μm membrane filter, and the filtrate was taken for PO₄³⁻ analysis.

Analytical methods

Orthophosphate concentrations were determined by the molybdenum–antimony anti-spectrophotometric method (National Environmental Protection Standards of the People’s Republic of China). The elemental analysis for the tailings was conducted using an X-ray fluorescence spectrometer (ARL-9800) and scanning electron microscope (S-3400N).

RESULTS AND DISCUSSION

Phosphate adsorption isotherm

The results of the phosphate adsorption isotherm experiments are shown in Figure 2. The experimental isotherm data can be characterized by the typical L-curve isotherm. The phosphate adsorption capacity considerably increased with the phosphate equilibrium concentration increasing from 0 to 10 mg P/L. This capacity was approximately 0.3 mg P/g tailings at the PO₄³⁻ equilibrium concentration of 10 mg P/L and pH 6.7. With a further increase of the PO₄³⁻ equilibrium concentration, the increase of the adsorption capacity was less significant. The Freundlich and Langmuir isotherms were used for fitting the experimental data.

Freundlich equation: \[ q = KC^{1/n} \] (1)

Langmuir equation: \[ q = \frac{bq_mC}{1 + bC} \] (2)

where \( q \) is the amount adsorbed at equilibrium (mg/g), and \( C \) is the equilibrium concentration in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data.

In this study, the isotherm data from Figure 2 were fitted to the Freundlich and Langmuir models. The estimated model parameters with the correlation coefficient \( R^2 \) are shown in Table 2. The fitting curves from these two isotherms are also illustrated in Figure 2. It is shown that the experimental data of phosphate adsorption on this tailing material could be well fitted by these models. The applicability of the two-parameter isotherm models for the present experimental data approximately follows the order: Langmuir > Freundlich.

Phosphate adsorption kinetics

The results of phosphate adsorption kinetic experiments at 20, 30 and 40°C are shown in Figure 3. It can be seen that the adsorption rate was slightly higher at a higher temperature. However, the majority of P adsorption on lead-zinc tailings at 20–40°C was completed in 20–30 min. For example, after 10, 20 and 30 min of adsorption, the adsorbed phosphate at 30°C was, respectively 59, 72 and 79% of that at 2 h.

The P adsorption kinetic data (Figure 3) were fitted with the kinetic models of the simple Elovich equations \( q = a + b\ln T \). The simple Elovich equations and estimated parameters with \( R^2 \) are shown in Table 3. The fitting curves resulting from the simple Elovich equations are plotted in

---

**Table 2** | Estimated isotherm parameters for phosphate adsorption on lead-zinc tailings

<table>
<thead>
<tr>
<th>Langmuir equation</th>
<th>Freundlich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m ) (mg P/g)</td>
<td>0.35</td>
</tr>
<tr>
<td>( b ) (L/mg P)</td>
<td>0.657</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9996</td>
</tr>
<tr>
<td>( K )</td>
<td></td>
</tr>
<tr>
<td>( 1/n )</td>
<td></td>
</tr>
<tr>
<td>( R^2 )</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. It is apparent that the simple Elovich equations could provide satisfactory fitting of the kinetic data of phosphate adsorption on the tailings. This high applicability of the simple Elovich equation for the present kinetic data is generally in agreement with other researchers’ results that the Elovich equation was able to describe properly the kinetics of phosphate adsorption on soils and soil minerals (Chien & Clayton 1980).

Effect of pH on phosphate adsorption by the lead–zinc tailings

The pH of the aqueous solution is an important variable that influences the adsorption of anions and cations at the solid–liquid interfaces. The effect of pH on phosphate adsorption on the lead–zinc tailings for pH between 2.05 and 12.52 is presented in Figure 4. It can be found that phosphate adsorption tends to decrease with the increase of pH, from 0.37 mg P/g at pH 2.05 to 0.12 mg P/g at pH 7.01, and tends to increase with the increase of pH, from 0.12 mg P/g at pH 7.01 to 0.64 mg P/g at pH 12.52. The results of the effect of pH on adsorption capacity show that the adsorption capacity of lead–zinc tailings is strongly dependent on solution pH and several reasons may be adduced to this. First, the change of surface characteristics can affect adsorption capacity to some extent. The surface characteristics of lead–zinc tailings, such as the surface charge changes from positive to negative as pH increases. The increase of OH\(^-\) in solution could affect the electrostatic properties of the lead–zinc tailings. The adsorption of OH\(^-\) on the surface of the lead–zinc tailings leads to the formation of a new charged layer, making the lead–zinc tailings surface have a comparably lower affinity to phosphate. With an increase in pH, OH\(^-\) competes strongly with phosphate for active sites, which affects the adsorption capacity. This therefore implies that adsorption is favored by low pH values and that adsorption capacity would be higher at low pH values than at high pH values. So phosphate adsorption tends to decrease with the increase of pH, from 0.37 mg P/g at pH 2.05 to 0.12 mg P/g at pH 7.01. This agrees with many reports from previous researchers (Yeoman et al. 1988; Agyei et al. 2002). Second, solubility diagrams for metal phosphates in pure water show that when iron and aluminum are present, strengite (FePO\(_4\)) and varisite (AlPO\(_4\)) are the stable solid phases in the low pH range (<6.5). At higher pH (>6.5), the iron and aluminum chemistry becomes increasingly governed by the formation of oxides and hydroxides, and these conditions are more ideal for the precipitation of phosphate with calcium as apatites and hydroxyapatites (Grubb et al. 2000). So phosphate adsorption tends to increase with the increase of pH, from 0.12 mg P/g at pH 7.01 to 0.64 mg P/g at pH 12.52.

The lead–zinc tailings contained Fe\(_2\)O\(_3\) (7.28%), Al\(_2\)O\(_3\) (3.88%) and CaO (20.58%) as shown in Table 1. As mentioned before, the actual phosphate removal on the tailings could be a consequence of adsorption and precipitation reactions with Fe, Al and Ca; the trend that the capacity of phosphate removal decreased with increased pH (<6.5)
suggests that precipitation with Fe, Al should be a significant process responsible for phosphate removal by the lead–zinc tailings; the trend that the capacity of phosphate removal increased with increased pH (>6.5) suggests that precipitation with Ca should be a significant process responsible for phosphate removal by the lead–zinc tailings. As a result, adsorption of phosphate mainly on calcium oxides is likely the key mechanism for phosphate removal using the present tailings material.

The results of phosphate adsorbed on the lead–zinc tailings were tested with an X-ray fluorescence spectrometer (see Table 1). According to the results in Table 1, the content of phosphorus pentoxide adsorbed on the lead–zinc tailings is 0.21%, but the content of phosphorus pentoxide in the present tailings material is 6.5).

4. The results of phosphate adsorbed on the lead–zinc tailings were tested with an X-ray fluorescence spectrometer. The tests demonstrated that the lead–zinc tailings are an effective adsorbent for phosphate removal. Due to their low cost and high capability, the lead–zinc tailings have the potential to be utilized for cost effective removal of phosphorus from wastewater.

5. It was demonstrated that the lead–zinc tailings are an effective adsorbent for phosphate removal. Due to their low cost and high capability, the lead–zinc tailings have the potential to be utilized for cost effective removal of phosphorus from wastewater.

CONCLUSIONS

Phosphate removal from aqueous solutions was studied using lead–zinc tailings. Based on the results of this study, the following conclusions can be drawn.

1. The isotherm data were well fitted with Langmuir and Freundlich isotherm models by non-linear regression. The applicability of the used two-parameter isotherm models for the present phosphate adsorption data approximately followed the order: Langmuir > Freundlich.

2. The initial phosphate adsorption on the tailings was rapid and the adsorption rate was slightly higher at a higher temperature between 20 and 40°C. The adsorption kinetics could be best described by the simple Elovich equation.

3. Phosphate adsorption tends to decrease with the increase of pH, from 0.37 mg P/g at pH 2.05 to 0.12 mg P/g at pH 7.01, and tends to increase with the increase of pH, from 0.12 mg P/g at pH 7.01 to 0.64 mg P/g at pH 12.52. The trend that the capacity of phosphate removal decreased with increased pH (<6.5) suggests that precipitation with Fe, Al should be a significant process responsible for phosphate removal by the lead–zinc tailings; the trend that the capacity of phosphate removal increased with increased pH (>6.5) suggests that precipitation with Ca should be a significant process responsible for phosphate removal by the lead–zinc tailings.

REFERENCES


First received 30 June 2012; accepted in revised form 9 October 2012