Recovery of phosphorus from sewage sludge in combination with the supercritical water process
Yunbo Zhai, Bobin Xiang, Hongmei Chen, Bibo Xu, Lu Zhu, Caiting Li and Guangming Zeng

ABSTRACT

In this paper, the fraction transformation and recovering of phosphorus (P) from sewage sludge (SS) residues, derived from supercritical water process, was investigated by extraction and precipitation processes. In addition, the form of heavy metals existing during the recovery process is also discussed. First, P in the solid residues was recovered by acid leaching with HCl, and then the derived P was adsorbed by activated alumina (Al2O3). Finally, the Al2O3 was desorbed with low concentration of NaOH. Results showed that 80% organic P was converted into HCl-P. The total P (the chief ingredient of HCl-P) in solid residue increased from 86.1 to 95.6% as temperature increased from 350 to 400 °C. The amount of P in the solid residue that was dissolved by 1 M HCl was 97.8%, and over 95% of P in the leaching solution (15 mg/L for P concentration) was adsorbed after 5.0 g of Al2O3 powder was added. The amount of P desorbed from Al2O3 with 0.1 M NaOH was 98.7%. Ultimately, over 85% of TP in SS was recovered. Moreover, the proportion of Cu, Zn and Pb in the extracted P products was lower than 5%.

Key words | activated alumina, extraction, phosphorus recovery, sewage sludge, sub/super-critical water reaction

INTRODUCTION

Phosphorus (P), an important element of nature, makes a significant contribution to the development of agriculture and industry. Phosphorus mines worldwide produced approximately 210 million tons of phosphorus rock concentrate in 2012 (Liu et al. 2007). As P is a non-renewable resource, the phosphate rock on the planet was estimated to meet human needs for only 50–100 years (Driver et al. 1999). Therefore, recovering P from P-rich resources is particularly important.

In 2012, the sludge production of China was as much as 24.186 million tons and contained about 125,000 tons of P (http://www.mep.gov.cn/). In recent years, many studies concentrated on the recovering of P from sewage sludge (SS) for its high P content. Directly utilizing the treated SS in agriculture represents a simple and effective means of applying P and other nutrients to crops, but the potential harm of direct use of SS has been found (McGrath et al. 1988). Feeding animals with the plants growing in sludge soil may lead to the accumulation of Cd or Pb in liver or kidney (Hillman et al. 2003). Xu et al. (2012) found that the cation exchange resin was responsible for removal efficiency of the heavy metals from P-rich solution. In addition, orthogonal tests showed that the optimal parameters for P precipitation are a molar ratio of Mg:N:P as struvite of 1.6:1.6:1 and pH at 10. The methods mentioned above describe the usage of the raw SS. However, there are still plenty of shortcomings such as heavy metal contamination, organic toxicants and low P recovery efficiency (Kuroda et al. 2002). So a better method for recovering P from SS needs to be studied and put forward.

The supercritical water (SCW) reaction (temperature >374.15 °C, pressure >22.1 MPa) is investigated due to its outstanding characteristics including the removal of chemical oxygen demand and effective recovery of fuel (Zhai et al. 2014). But the majority of researchers ignored the high concentration of P in SS; only a few studied the transformation and possible recovery method of P during SCW reaction. Levlin (2007) performed a two-step leaching process whereby acid and sodium hydroxide were added into subcritical water oxidation residues in order, and 60% of total P...
(TP) and low concentration of Ca and Al were recovered. How to find a reliable method to recover pure P from sludge residue and reduce the energy consumption are some other important problems. Thus, the aim of this paper is to find a simple and effective method to extract P from SCW residues and reduce energy usage.

**MATERIALS**

The experimental equipment is a 0.5 L batch autoclave reactor. SS used in this experiment is the secondary municipal SS from Guozheng Sewage Treatment Plant in Hunan province, southern China. The SS was dried in a drying stove at temperature of 105 °C for 24 h, and then it was pulverized and sieved to make sure the sludge particle size was in the range of 0.2–0.5 mm. The chemical characteristics of the sludge, shown in Table 1, were determined using a thermo gravimetric analyzer (STA 409 model; Netzsch, Germany) and a 2400 Series II CHNS analyzer (PerkinElmer, Waltham, MA, USA). The Al₂O₃ was purchased from Tianjin Bohong Resin Technology Co., Ltd, Tianjin, China. Two types of Al₂O₃ were used: granular Al₂O₃ (diameter 2–3 mm) and powder Al₂O₃ (<200 mesh).

**METHODS**

**SCW reaction of SS**

In this study, 17 g of dewatered sludge and 153 mL of distilled water were put into a reaction kettle. Then the reactor was heated up to a pre-set temperature (350 or 400 °C) by a 4.0 kW electric furnace (average heating rate of 3.4 °C/min), and once the set temperature was reached, the highest temperature was kept for 30 min. Then the reaction kettle was cooled down by circulatory cooling water. After that, the products were collected: the solid residue and liquid products were separated by sand filter funnel, pure oil products in solid and liquid product were extracted with dichloromethane and solid product was washed with water and dried at 105 °C for 12 h.

**P analysis of SS during SCW reaction**

First, all the liquid volumes of products were adjusted to 500 mL by the addition of distilled water, as their volumes were not the same after SCW reaction. Secondly, the pH value and TP concentrations of the diluted liquid products were analyzed, and the fractions of P in the raw SS were analyzed. Then the concentrations of TP-350 °C (TP of residues from reaction conducted at 350 °C, 22.0 MPa) and the rest of the P fraction were investigated too. Moreover, the same procedures performed in SCW residues with reaction condition of 400 °C and 31.2 MPa were also investigated. The TP, inorganic P (IP), organic P (OP), NaOH-P (phosphorus complex with Al, Fe, Mn and their hydroxide) and HCl-P (phosphorus mainly complexed with calcium phosphate) were analyzed according to the Standard Measurement and Testing (SMT) protocol (Ruban et al. 2001). The extraction methods are shown in Table 2.

**P extraction and recovery**

First, the HCl-P solution, which was obtained by adding 1 mL HCl (1 M) per 1.0 mg SCW residues, was diluted to different concentrations (15 and 50 mg/L) with water. Secondly, heavy metal concentrations of HCl-P solution were measured by AAnalust-700 atomic absorption

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Contents of main elements and chemical characteristics of SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate analysis</td>
<td>Contents (wt%)</td>
</tr>
<tr>
<td>M</td>
<td>87.62</td>
</tr>
<tr>
<td>VM</td>
<td>60.2</td>
</tr>
<tr>
<td>A</td>
<td>39.8</td>
</tr>
<tr>
<td>FC</td>
<td>6.8</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calorific value (KJ/kg): 16610</td>
<td></td>
</tr>
</tbody>
</table>

M: moisture; VM: volatile matter; A: ash; FC: fixed carbon.
spectrometer (PerkinElmer, USA). Thirdly, studies on P recovery by Al₂O₃ were conducted on the HCl-P solution. Moreover, effects of pH value, concentration of P, Al₂O₃ size (granular and powder) and dosage of Al₂O₃ on the recovery were investigated. The diluted NaOH solution (0.1 M) was used to release the P from Al₂O₃; the release rate was obtained by detecting the concentration of P in the solution after the adsorption process. Finally, in the processes of absorption and desorption, the concentrations of heavy metal (Cu, Zn, Cr, and Pb) were determined.

Table 2 | Phosphorus sequential extraction by SMT

<table>
<thead>
<tr>
<th>Categories of P</th>
<th>Extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>The 250 mg sample was burned for 3 h at 450 °C, then extracted with 20 mL HCl (3 M), and oscillated at constant temperature for 16 hours, and finally centrifuged and tested by spectrophotometric method.</td>
</tr>
<tr>
<td>IP</td>
<td>The 250 mg sample was added to 20 mL HCl (1 M); the following operation was the same as for TP.</td>
</tr>
<tr>
<td>OP</td>
<td>The dried residue from IP was burned for 3 h at 450 °C, then extracted with 20 mL HCl (1 M); following operation was the same as for TP.</td>
</tr>
<tr>
<td>NaOH-P</td>
<td>The 250 mg sample was extracted with 20 mL NaOH (1 M), oscillated for 16 h and centrifuged; then 10 mL of the supernatant was poured into 5 mL HCl (3 M), finally centrifuged and tested.</td>
</tr>
<tr>
<td>HCl-P</td>
<td>The residue from NaOH-P was washed by NaCl solution, centrifuged and poured into 20 mL HCl (1 M); the following operation was the same as for TP.</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Conversion and distribution of P during subcritical and supercritical water reactions

The fraction of P in raw SS (no chemical P removal) is illustrated in Figure 1. The content of TP is 11.4 ± 0.1 mg/g, accounting for 1.14% of the total mass of the sludge, and the content of IP and OP is 8.34 ± 0.1 mg/g and 2.94 ± 0.05 mg/g respectively.

Tremendous changes in the composition of phosphorus occurred during the subcritical and supercritical water reactions. The results showed that TP was greatly enriched in SCW residues by the SCW reaction, most of the TP was transferred into the solid residues and the rest of the P (about 4.4%) was dissolved in the aqueous phase. The concentration of TP increased from 26.8 to 27.91 mg/g when reaction condition changed from 350 °C, 22.0 MPa to 400 °C, 31.2 MPa. Results showed that the TP concentration of SCW residues (400 °C, 31.2 MPa) was 2.4 times higher than the concentration of TP in raw sludge. This may be due to the removal of organic materials and the production of insoluble P products after SCW reaction. Figure 1 also shows that the concentration of IP-350 C and HCl-P-350 C is 25.65 and 25.33 mg/g. Correspondingly, the concentration of OP-350 C and NaOH-P-350 C is 0.96 and 0.26 mg/g as TP is composed of OP, HCl-P and NaOH-P according to the extraction methods of P (in Table 2). But when the reaction temperature increases to 400 °C, the concentration of HCl-P-400 °C, OP-400 °C, and NaOH-P-400 °C is 27.51, 0.43 and 0.12 mg/g respectively. Thus, the content of HCl-P in the SCW residues gradually increased as the temperature increased, and the content of NaOH-P reduced.
This meant HCl-P was a more stable form in the SCW reaction. According to the research of Yanagida et al. (2007) HCl-P existed completely as hydroxyapatite; the produced HCl-P had migrated into the solid residue as HCl-P had a lower solubility than NaOH-P after SCW reaction. Possible reactions are described in the following equations (Zhu et al. 2011):

\[
M_{3-m}(H_mPO_4)_b \rightarrow (3 - m)M^{b+} + b(H_mPO_4)^{m-3} \\
m = 0, 1, 2
\] (1)

\[
M = Al^{3+}, Fe^{3+}, Mn^{2+} \ldots \text{except for } Ca^{2+}
\]

\[
2(H_mPO_4)^{m-3} + (3 - m)Ca^{2+} \rightarrow Ca_{3-m}(H_mPO_4)_2 \downarrow \\
m = 0, 1, 2
\] (2)

It can be inferred that OP occurred due to a similar reaction. The OP was broken down into phosphate ion and other components by supercritical reaction and then formed calcium phosphate precipitate by combining with Ca\(^{2+}\).

**Effect of pH and Al\(_2\)O\(_3\) performance for P extraction**

The Al\(_2\)O\(_3\) was applied for extraction of P in the HCl-P solution, as it has a high adsorption capacity for P (Hano et al. 1997). In this experiment, over 95% of P was extracted when the pH value was below 4. But with the continuing increase of pH, the extraction of P was greatly decreased. Results indicated that P could be extracted in the form of anion. The widely accepted mechanisms for P extraction are shown in Equations (3) and (4) (Urano & Tachikawa 1991).

\[
Al_2O_3 + 3H_2O \rightarrow Al(OH)_3 
\] (3)

\[
2Al(OH)_3 + H_2PO_4^- \rightarrow AlPO_4 + OH^- + 2H_2O 
\] (4)

According to the equations above, the phosphorus adsorption by activated alumina would produce OH\(^-\); so phosphorus adsorption could be enhanced under acidic conditions and the adsorption amount decreased with the increasing pH value. Therefore, the pH of leaching solution did not need to be adjusted during the actual extraction and recovery procedures.

![Figure 2](https://iwaponline.com/wst/article-pdf/70/6/1108/470644/1108.pdf)

**Figure 2** | Effects of Al\(_2\)O\(_3\) performance on P extraction.
Figures 2(a)–(d) show the extraction capacity of two forms of Al₂O₃ (spherical and powdered) in IP concentrations are 15 and 50 mg/L, respectively. According to the study, for the same dosage and P concentrations, the extraction capacity of spherical Al₂O₃ (4.1 mg/g) was significantly lower than that of the powdered Al₂O₃ (6.2 mg/g). When the concentration of P in the leaching solution was 50 mg/L and the equilibrium concentration was not limited, the extraction capacity of spherical Al₂O₃ was 7.7 mg/g, and the capacity of Al₂O₃ powder increased to 15.4 mg/g. One possible reason was that the diameter of a phosphate molecule was larger than the pore diameter of the solid Al₂O₃, which was contrary to the extraction of phosphate ions. So it was necessary to design and manufacture a suitable Al₂O₃ extractant.

Another important influence on recovering P was the concentration of the soluble P. As can be seen from Figure 2, the Al₂O₃ showed a good performance for extracting soluble P. In a low P concentration (about 15 mg/L), the extraction capacity could be up to 6.2 mg/g and the equilibrium concentration was 0.2 mg/L. The extraction capacity increased with increasing concentration of P; hence choosing a suitable dosage of Al₂O₃ would have a significant impact on the P recovery efficiency.

**P recovery and activated alumina regeneration**

A process based on the acid leaching and Al₂O₃ extraction of P was designed according to Figure 3. Nearly 100% P had been leached with HCl, and similar results were found in Kristina Stark’s experiments (Stark 2006). The leaching solution of SCW solid residues and aqueous phase after SCW reaction were mixed to maximize the recovery rate of P. Then, the pH of mixed solution was adjusted by distilled water and 1 M NaOH. Al₂O₃ showed a good performance of desorption at low concentrations of NaOH solution according to Chen et al. (2006). The result showed that 98.7% of P absorbed had been dissolved from Al₂O₃. Finally, the P had been recovered in the form of calcium phosphate precipitate by adding an appropriate amount of calcium hydroxide solution (Ca(OH)₂). Moreover, the hydrochloric acid, sodium hydroxide solution and desorbed Al₂O₃ were reused.

**The removal of heavy metals during P recovery**

The elemental analysis of sludge (Table 1) showed that the dry sludge had relatively high levels of Cr, Zn, Cu, Pb and As. During the recovery processes of Figure 3, the concentrations of Cu, Cr, Zn, Pb were measured during the adsorption process. At pH = 2, the adsorption efficiency of Cu, Zn, Cr and Pb was 11.4, 30, 92.8, and 19.9% respectively. The Al₂O₃ had a strong adsorption effect on Cr, while the adsorption effects on the other three heavy metals were poor. This was because the Cu, Cr, Zn, and Pb were adsorbed on the outer layer of Al₂O₃. Also Cu, Zn and Pb were in cationic form in solution, and the positively charged cation could access the surface of Al₂O₃ more easily; so the adsorption efficiency of the three heavy metals was less than 30% (Naiya et al. 2009). Cr in acidic
solution existed in the form of CrO$_2$$^4$ and HCrO$_4$; the adsorption efficiency reached 94.15% in the case of pH = 2. The results also showed that the adsorption efficiency of Cu and Pb were higher than 90% in the case of pH ≥ 9. The reason may be that the Al$_2$O$_3$ surface positive charge increased with the increase of pH, and the cationic from could easily access the Al$_2$O$_3$ surface. On the other hand, the high pH would lead to hydroxide precipitation. In contrast, the increase of pH resulted in the decrease of the removal rate of Cr. The removal rate of Cr was less than 20% when pH > 10. The reason for this was the decrease of positive charge on the surface of Al$_2$O$_3$, which resulted in the decrease of adsorption amount of CrO$_2$$^4$ and HCrO$_4$$^-$. The removal efficiency of Zn also highly depended on the hydrogen ion concentration in solution. It can be noted that the optimal pH value of adsorption of Zn(II) was 5. The reason might be follows: at pH < 4, due to high positive charge density on the surface sites, high electrostatic repulsion would result in lower removal efficiency during uptake of metal ions.

The desorption of P was accomplished by 0.1 M NaOH. Results showed that the removal rate of Cu, Zn, Pb and Cr in desorption solution was 94.3, 97.4, 92.3 and 19.5%. In addition to the chromium in the solution exceeding 10 mg/L, Cu, Zn and Pb desorption concentration in the solution was 1.3, 0.7 and 0.3 mg/L, not affecting the quality of the recovery of P.

**CONCLUSIONS**

Combining acid leaching of P and the adsorption of Al$_2$O$_3$ could efficiently extract P from SCW residues. First, the majority of P partitioned into the solid residues after SCW reaction, and TP in solid residues increased from 86.1 to 95.6% as the reaction temperature increased from 350 to 400 °C. Secondly, 97.8% of P in solid residue was dissolved by 1 M HCl. Over 95% of P in the solution was adsorbed when 5.0 g of powdered Al$_2$O$_3$ was added and P initiation concentration was 50 mg/L. Also 98.7% of P was dissolved from Al$_2$O$_3$ when 0.1 M NaOH was added. Moreover, the removal rates of Cu, Zn, Pb and Cr in recycle production were 92.53, 94.87, 93.62 and 19.53% respectively during the desorption process. Ultimately, over 85% of TP in SS was recovered. Therefore, with simple procedures, a small amount of resources consumed could obtain a purer product of P. In addition, extraction capacity of granular and powdered Al$_2$O$_3$ for P showed great difference; so further study must focus on a better manufacturing method of the Al$_2$O$_3$ sorbent to achieve better absorption efficiency.

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**REFERENCES**


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