Evaluation of phosphorus removal from wastewater by soils in rural areas in China

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Abstract

Low-cost, easy-maintenance and high-efficiency decentralized wastewater treatment technologies are urgently needed in rural areas of China. Processes with high potential for phosphorus removal are of great interest. However, commonly used treatment methods often do not meet the strict criteria for removing phosphorus from rural wastewater. In order to search an economic and simple technology for phosphorus removal from the common bio-technologies effluent, seven soil types collected from different rural areas in China were investigated for their ability to remove phosphorus. X-ray diffraction (XRD) was used to analyse the mineral structure, and inductively coupled plasma optical emission spectrometer (ICP-OES) was used to analyse the geochemical composition of the soil samples. Three primary minerals – quartz, albite and montmorillonite – were clearly detected. The samples were divided into two soil types, acidic soils and alkaline soils, based on their pH values. The geochemical composition study indicated that a higher percentage of Ca and Mg occurred in alkaline soils (pH > 8) than in acidic soils (pH < 6.5). Adsorption isotherms from batch experiments fitted the Langmuir and Freundlich models well, the maximum P adsorption capacities ranged from 0.256 to 1.598 mg P/g, indicating a high phosphorus removal potential for all of these soils. The P fractions extracted revealed that the sum of NaOH-extracted inorganic P (NaOH-Pi) was the major P component in the acidic soils, and CaCO3-bound phosphorus (Ca-P) in the alkaline soils. Dynamic adsorption simulation showed that these soils have the ability to remove phosphorus from wastewater.

Key words: adsorption; phosphorus removal; rural areas; wastewater treatment
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Introduction

The quantity of domestic wastewater has sharply increased in recent years with the economic development of some rural areas in China. Almost all the wastewater is discharged directly into the aquatic environment due to shortage of decentralized wastewater treatment systems. Phosphorus in wastewater can lead to eutrophication of the receiving water bodies (Oguz et al., 2003). Therefore, Chinese governments have issued strict standards for P-concentration control in the effluent of wastewater treatment plants to avoid more and more rivers and lakes suffering the fate of Taihu Lake and Chaohu Lake in the Yangtze-Huaihe region, notorious for their eutrophication (Jin et al., 2005).

Septic tanks have been extensively used for domestic wastewater disposal in rural areas in China. However, the concentration of suspended solids (SS), biochemical oxygen demand (BOD), total nitrogen (TN) and total phosphorus (TP) in effluents from septic tanks do not meet the standard (Fox, 1984). Septic tanks generally play only a primary wastewater treatment role, and should be followed by an aerobic treatment process. However, the fact is that conventional biological wastewater treatments do not remove phosphorus very effectively, and sorption methods using various types of natural and synthetic materials to remove phosphorus have been widely studied.

Mesoporous zirconia (ZrO2) is one synthetic material that has been found to remove phosphorus from aqueous solutions (Liu et al., 2008) and therefore has the capacity for controlling phosphorus pollution. Among natural materials, sand has been observed to act as a sorbent for phosphorus in constructed reed beds (Arias et al., 2001; Bubba et al., 2003). Many researchers (Ugurlu and Salman, 1998; Khelifi et al., 2002; Agyei et al., 2000, 2002; Grubb et al., 2000; Cheung and Venkitachalam, 2000; Sakadevan and Bavor, 1998; Johansson, 1999; Johansson and Gustafsson, 2000; Oguz, 2004) have all reported that fly ash and/or slag are highly efficient media for removing phosphorus in filtration and constructed wetland systems. Clay minerals and soils such as reactive Ca, Fe and Al have also been shown to strongly adsorb phosphorus, the efficiency depending on their composition (Yuan et al., 2005). Thus, there is evidence that many materials can remove phosphorus from solution.

The concentrations of COD, BOD, SS and TN in the effluent of biological systems are often less than 40, 20,
1.3 Mineralogical and physicochemical properties of saturated adsorption experiments. The synthetic wastewater (COD 50 mg/L, BOD 20 mg/L, NH4+-N 8 mg/L, TN 20 mg/L, TP 5 mg/L, and pH range 6–8) simulating typical effluent from biological wastewater treatment systems without phosphorus removal. In order to investigate the adsorption mechanism, a KH2PO4 solution was used as an adsorbate in the adsorption isotherm and adsorption column experiments were used to evaluate the phosphorus removal properties of soils from different rural areas of China.

1 Materials and methods

1.1 Soil samples

All of the soil samples were collected in 2007 from the rural areas in China. One sample each was taken from northeastern, eastern and southwestern China, and four samples were collected in northern China. These were labelled Haerbin (HE), Jiaxing (JX), Lijiang (LJ), Beijing (BJ), Tianjin (TJ), Taiyuan (TY) and Xinxiang (XX). Prior to analysis, for homogeneity all samples were air-dried and passed through 20-mesh and 100-mesh sieves.

1.2 Test wastewater

The feed liquid in the dynamic column experiments was synthetic wastewater (COD 50 mg/L, BOD 20 mg/L, NH4+-N 8 mg/L, TN 20 mg/L, TP 5 mg/L, and pH range 6–8) simulating typical effluent from biological wastewater treatment systems without phosphorus removal. In order to investigate the adsorption mechanism, a KH2PO4 solution was used as an adsorbate in the adsorption isotherm and saturated adsorption experiments.

1.3 Mineralogical and physicochemical properties of raw soil samples

The mineral component of the soil was analyzed by a X-ray diffraction (XRD) using CuKα radiation (λ = 0.15418 nm, 40 kV, 100 mA) and JADE Version 5.0 software for diffractogram analysis and to calculate the percentages of minerals components. Organic matter (OM), pH and available P were measured using techniques described in the literature (Bao, 2000). Specific surface area of the raw soil samples were measured by the BET method (ASAP 2000 short for Accelerated Surface Area and Porosimetry, Micromeritics Co., USA). For total metal analysis, the raw soil samples were digested with a 5:1 mixture of hydrofluoric acid and perchloric acids (Tessier et al., 1979). The Fe, Al, Ca, Mg, Mn amounts in the solution were then measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 2000DV, PerkinElmer Co., USA). Amorphous and poorly crystalline iron, aluminium, and Mehlich I-calcium and magnesium quantities were determined using oxalic acid-ammonium oxalate and Mehlich I extraction methods, respectively (Pierzynski, 2000). The samples were mixed with specific acidic extraction solution in fixed proportions of weight/volume, and then continually shaken in a reciprocating shaker at constant temperature and rotational speed. The extracts were then filtered through a 0.45-μm filter paper and the filtrate analyzed for metals content by ICP-OES.

The soil particle sizes were determined using the simplified method of Kettler et al. (2001): 3% sodium hexametaphosphate (HMP, (NaPO3)6) was mixed with soil in the ratio 3:1 (W/W) and the solution shaken for 2 hr on a reciprocating shaker at 120 r/min. The sand fraction was collected on a 0.053-mm sieve and the silt and clay fractions were allowed to settle at temperatures 18–24°C for 3 hr. After this time the suspended clay fraction was decanted from the settled silt particles and transferred into a pre-weighed container, and the silt was transferred into another pre-weighed container. Both containers were then dried at 105°C to constant weight.

1.4 Adsorption isotherms

Triplicate 1.0 g samples of each soil were accurately weighed, then transferred into 100 mL polyethylene centrifuge tubes with different amounts of P as KH2PO4 solution, including 25 mL of 0.01 mol/L KCl to adjust the ionic strength. Two drops of chloroform were added to each tube to prevent bacterial growth. Ten initial phosphorus concentrations (0, 0.1, 1, 2, 10, 20, 40, 50, 80, 100 and 200 mg P/L) were utilized. The centrifuge tubes were then shaken continuously at 190 r/min and 25°C for 48 hr, by which time the adsorption was considered to be approximately at equilibrium. The supernatant was extracted from the solution with polyethylene syringes for filtration through a 0.45-μm filter paper. Total phosphorus was then determined by ascorbic acid colorimetric with a spectrophotometer (Greenberg et al., 1992). The quantity of the adsorbed phosphorus in the soil was then equated with the decreased amount of phosphorus in solution.

The results of these batch experiments were analyzed by the Langmuir (Eq. (1)) and Freundlich (Eq. (2)) equations:

\[ q_e = \frac{bQ}{1 + bC_e} \]  
\[ q_e = KC_e^{1/n} \]

where, \( q_e \) (mg/kg) is the quantity absorbed on sorbent; \( C_e \) (mg/L) is the equilibrium concentration in solution. The other parameters are isotherm constants determined by regression of the TP sorption data (Zeng et al., 2004).

1.5 Adsorption saturation studies

Duplicate 10.0 g samples of each soil were accurately weighed and placed in 100 mL polyethylene centrifuge tubes with a solution having an initial phosphorus concentration of 500 mg P/L as KH2PO4, and 50 mL of 0.01 mol/L KCl was added. The sealed tubes were then continuously shaken at 25°C and 190 r/min until the supernatant phosphorus concentration was approximately at equilibrium. The phosphorus equilibrium concentration was analyzed
as above. The supernatants were carefully removed and the solids were air-dried preparatory to analysis. The raw soil samples were analyzed for TP by the HClO₄-H₂SO₄ digestion method (Bao, 2000).

The TP amount of the adsorption saturation samples was the sum of TP in raw samples plus adsorbed phosphorus. The P fractions in both the adsorption saturation samples and raw soil samples were determined by the fractions extracted method (Moore and Reddy, 1994; Pierzynski, 2000). The P fractions extracted were exchangeable P (KCl-P, extracted by 1 mol/L KCl), iron/aluminum-bound P (NaOH-Pi, extracted by 0.1 mol/L NaOH, spectrophotometry directly), organic-bound P (NaOH-Po, extracted by 0.1 mol/L NaOH, the difference between digestion and no-digestion), calcium-bound P (Ca-P, extracted by 0.5 mol/L HCl) and residual P (Res-P, calculated by the difference with TP). The morphology and microstructures of the raw and adsorption saturation samples were observed with a scanning electronic microscopy (SEM) and energy dispersive X-ray (EDX) (S-3000N, Hitachi, Japan).

1.6 Dynamic column experiments

Three representative soils were selected from the seven raw soil samples for the dynamic column experiments to evaluate the practicality of removing phosphorus from the effluent of a biological treatment unit. The soils were mixed with stone-pebbles (3–8 mm in diameter) in the ratio 3:1 (W/W) (Oladoja and Ademoroti, 2006). The mixture was then packed into a column of length 40 cm and 5 cm diameter (Fig. 1). The uniform weight of each of the three samples ensured close to identical filtration lengths. The influent was continuously pumped through a plastic tube connected to a BT100-1L variable-speed peristaltic pump. The synthetic wastewater was allowed to pass through the mixture by gravity flow. The filtrate was collected and analyzed as in Section 1.3 above to determine TP concentration changes in the effluent.

2 Results and discussion

2.1 Physicochemical and mineralogical properties

All the soil samples were subdivided according to their pH: acidic soils LJ (5.45), JX (6.06) and HE (6.40), and alkaline soils BJ (8.05), TY (8.10), XX (8.16) and TJ (8.45) (Table 1). The background values of organic matter (OM), total phosphorus (TP) and available phosphorus in these seven soils are shown in Table 1. The OM value is an important indicator of soil fertility. In this study, the OM contents in JX, HE, TY, TJ were over 4.5%, indicating high fertility (Bao, 2000); however, the OM content of LJ (around 1%) was somewhat lacking in fertility. The OM value was not observed to be directly correlated with phosphorus sorption. The relationship between OM and phosphorus sorption was attributed to Fe and Al bound to OM (Fernandes and Warren, 1994). The available phosphorus content also indicates fertility in both acidic and alkaline soils. The available P in LJ was only 3.94 mg/kg, which was the lowest level of the acidic soils, although its TP content was the highest. Similarly, BJ was in the low fertility range according to the alkaline soil criteria.

The XRD analysis results are also shown in Table 1. Quartz and albite were abundant in all the soils, at 21%–33% and 13%–37%, respectively. Kaolinite content in LJ was 21% and in TJ was 36%, and below 10% the others. Hematite, with Fe₂O₃ as the major component was scarce, all below 1%.

The percentages of total metals, Fe, Al, Mg, Ca and Mn in different soil samples were distinctly diverse as shown in Table 2. Alkaline soils contained more Ca and Mg than acidic soils; in particular, there was a positive correlation between Ca content and pH values throughout.

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>OM (%)</th>
<th>TP (mg/kg)</th>
<th>Available P (mg/kg)</th>
<th>Quartz (%)</th>
<th>Albite (%)</th>
<th>Microcline (%)</th>
<th>Kaolinite (%)</th>
<th>Chlorite (%)</th>
<th>Calcite (%)</th>
<th>Hematite (%)</th>
<th>Anatase (%)</th>
<th>Montmorillonite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LJ</td>
<td>5.45</td>
<td>1.1123</td>
<td>1192.91</td>
<td>3.9427</td>
<td>25</td>
<td>16</td>
<td>&lt; 1</td>
<td>21</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>9%</td>
<td>29</td>
</tr>
<tr>
<td>JX</td>
<td>6.06</td>
<td>4.9529</td>
<td>929.98</td>
<td>35.4844</td>
<td>29</td>
<td>26</td>
<td>7</td>
<td>4</td>
<td>8</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>6</td>
</tr>
<tr>
<td>HE</td>
<td>6.40</td>
<td>5.1544</td>
<td>438.21</td>
<td>20.0290</td>
<td>33</td>
<td>37</td>
<td>5</td>
<td>10</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>BJ</td>
<td>8.05</td>
<td>3.0242</td>
<td>662.18</td>
<td>3.6575</td>
<td>32</td>
<td>28</td>
<td>19</td>
<td>7</td>
<td>4</td>
<td>&lt; 1</td>
<td>Nil</td>
<td>Nil</td>
<td>8</td>
</tr>
<tr>
<td>TY</td>
<td>8.10</td>
<td>4.9664</td>
<td>708.44</td>
<td>22.9717</td>
<td>26</td>
<td>25</td>
<td>4</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>&lt; 1</td>
<td>Nil</td>
<td>6</td>
</tr>
<tr>
<td>XX</td>
<td>8.16</td>
<td>2.5838</td>
<td>691.40</td>
<td>6.0638</td>
<td>27</td>
<td>27</td>
<td>4</td>
<td>3</td>
<td>8</td>
<td>5</td>
<td>Nil</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>TJ</td>
<td>8.45</td>
<td>5.5958</td>
<td>657.32</td>
<td>13.4750</td>
<td>21</td>
<td>13</td>
<td>&lt; 1</td>
<td>36</td>
<td>8</td>
<td>12</td>
<td>Nil</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

OM: organic matter; TP: total phosphorus; Nil: zero.
The Ca percentage in TJ was more than 30 times that in LJ. The higher percentage of Ca could be explained by the high contents of calcite in alkaline soils. The percentages of Fe and Al in LJ were the highest among all soil types, however, the lower clinoclore it was. Oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}) have been considered to be positively correlated with phosphorus sorption in acidic soil and have been used to assess the capability for phosphorus adsorption of soil (Maguire et al., 2001). LJ, JX and HE were all acidic soils containing large amounts of oxalate-extractable Al and Fe. The correlation for Al_{ox} was higher than for Fe_{ox}; the capability for P adsorption can be seen when comparing Tables 2 and 4. The composition of Mehlich I-Ca was similar in the four alkaline soils; however, the amount of Fe_{ox} in TJ was far more than in BJ, TY and XX. The efficiency of phosphorus adsorption in Ca soil (alkaline soil) was determined by different factors. The high percentage of CaCO_3 and the rich levels of Fe_{ox} were both observed to have a positive correlation with the phosphorus sorption (Bertrand et al., 2003; Ryan et al., 1985). Although the percentage of calcite (CaCO_3) in BJ was much lower than in TJ, TY and XX (Table 1), the higher Fe_{ox} determined that its phosphorus adsorption capacity was close to that of TY and XX.

The results of the BET specific surface area analysis are shown in Table 3. The relationship between specific surface area and adsorption capability has been widely studied. It is the consensus that larger specific surface area can be beneficial to sorption by offering more adsorption sites to be utilized by adsorbate. LJ and TJ, with the largest specific surface areas (38.77 and 42.95 m^2/g, respectively), had the highest efficiency for removing phosphorus. In addition, the pore volume of TJ (0.0806 cm^3/g) was slightly larger than the pore volume of LJ (0.0616 cm^3/g). The specific surface area of the three alkaline soils BJ, TY and XX were less than 20 m^2/g, with XX having the lowest specific surface area (14.65 m^2/g). Although the specific surface area of HE was 34.80 m^2/g, its pore volume was low (0.0366 cm^3/g). This could be one reason why the phosphorus removal ability of HE was much weaker than that of LJ and TJ.

2.2 Adsorption isotherm and adsorption saturation studies

Table 2: Total metal, oxalic acid-ammonium oxalate Fe/Al and Mehlich I-Ca/Mg analysis

Table 3: Results of specific surface area analysis by BET

![Table 2](image1.png)

![Table 3](image2.png)

The data clearly fit these two models very well, indicating that they offer a credible method for evaluating the potential for P adsorption. With the Langmuir equation, the maximum P adsorption capacity (Q) was calculated from Eq. (1). The Q values for the acidic soil LJ and the alkaline soil TJ were the highest (> 1400 mg P/kg); acidic soils HE and JX belonged to the middle level; three alkaline soils, BJ, TY and XX were considered to have the lowest P sorption capability, with maximum P below 350 mg/kg. The values of b·Q (Eq. (1)) show the buffer capability when sorption takes place in a liquid-and-solid system (Yuan et al., 2005). In Fig. 2, the b·Q of LJ and TJ is higher than the other soils; HE, TY and XX had the lowest b·Q. That is to say, were the P concentration in the wastewater to suddenly fluctuate, the liquid-and-solid system of LJ and TJ would continue to remove phosphorus at high efficiency. The value of 1/n, one of the constants in Freundlich equation (Eq. (2)), did not show any distinct difference between the seven soil samples. When 1/n is in the range 0.1–0.5, the adsorbent is considered to be easy to adsorb (Zhang, 2000). Comprehensive consideration both of the two isotherms, the primary analysis resulted of the potential of removing phosphorus was evaluated: first level, TJ and LJ; middle level, HE and JX; lowest level, TY, BJ and XX.

In order to investigate the P forms and microstructures in soils after sorption, the adsorption saturation experiment was carried out. The P fractions of the raw samples and adsorption samples are shown in Table 4. The NaOH-Pi (Fe/Al-bound P) concentration rapidly increased in acidic soils LJ, JX and HE, and the increment of NaOH-Pi concentration was the majority in the increment of total phosphorus concentration with the percentages 82%, 89% and 90%, respectively. NaOH-Pi could be utilized as a source of available P if there was a deficit of phosphorus (Kuo et al., 2005). In acidic soils, NaOH-Pi could be enhanced through the P-removal process in wastewater treatment, meaning that the P fertility would also be improved. In alkaline soils, the major P form of the adsorbed phosphorus was calcium-bound P (Ca-P). As the Ca%
increased in raw alkaline soils, the percentage of Ca-P increment among the increment of total phosphorus was enhanced (BJ 48%, TY and XX 75%, TJ 88%). Since Ca-P is difficult to dissolve and relatively stable, using alkaline soil to remove P from wastewater is therefore considered suitable for fixing phosphorus where there is P loss. The increases in KCl-P, NaOH-Po and Res-P were not found to be significant in either acidic or alkaline soils.

SEM analysis results for the morphology and microstructure of the raw soils and their adsorption saturated samples are shown in Fig. 3. The surface structures of the soils were unchanged after the adsorption process. Neither crystalline existed was altered nor new crystalline was created after adsorption.

The EDX analysis results for LJ and TJ after the adsorption experiment are shown in Fig. 4. It was observed that Fe and Al were widely distributed in LJ where the phosphorus was nearby (Fig. 4a). In TJ (Fig. 4b), amounts of phosphorus can be observed adjacent to the Ca particles which can be found abundance in the image.

### 2.3 Performance efficiency of the dynamic column studies

The maximum P adsorption capacity calculated from the Langmuir and Freundlich models was based on batch experiments, in which the solution was static over extended contact times. The dynamic column experiment tested phosphorus removal efficiency for the case where the influent was continually flowing, simulating an actual long-term treatment process. Soil-particles are shown in Fig. 5. Soils in the dynamic column were chosen on the basis of their adsorption capacity and water permeability.
Compared with TJ, LJ had much more sand-particle, which means that the water permeability of LJ was much better than TJ, therefore, the acidic soil LJ was chosen as the representation of the first level in the dynamic column experiment. JX and XX were chosen as the representative adsorbents of the middle and lowest levels, respectively. The dry-weight of LJ, JX and XX was set at 100 g. The P concentrations in the effluent are shown in Fig. 6. According to class A of Chinese standard (GB18918-2002), the TP concentration in effluent should be < 0.5 mg/L. In this study, LJ was proved to have the best capability for phosphorus removal from the wastewater as estimated by Langmuir and Freundlich models, of which the TP concentration could be below the standard line until the day 22 with the volume of effluent 20 L. The breakthrough points of JX and XX were at day 17 with 7.5 L and day 5 with 3.5 L treated wastewater (Fig. 6), respectively.

3 Conclusions

Mineralogical analysis indicated an abundance of quartz and albite in all seven soils. The percentages of kaolinite were low except in LJ and TJ. Hematite, in which Fe₂O₃ was the major component, was scarce in these soils. LJ, JX, HE were acidic soils, the other four, BJ, TY, XX and TJ were alkaline. The contents of Ca and Mg in alkaline soils are higher than those in acidic soils. The BET specific surface areas of LJ and TJ were larger than others, and BJ, TY, XX own the smallest BET specific surface area. In acidic soils, Al₉₀ and Fe₉₀ were the major determinants of P sorption. The capability of P adsorption was determined by the interaction of the percentage of CaCO₃ and rich degree of the Fe₉₀ in alkaline soils. The contents of OM in these soils did not have direct correlation with the P sorption.

The P adsorption isotherms of all these soils fitted very well with both the Langmuir and Freundlich isotherm models. The maximum P adsorption capability was estimated to lie between 256 and 1598 mg P/kg. LJ and TJ had the best capability of P adsorption, JX and HE took the second place, BJ, TY and XX were in the last level. The results of P fractions and SEM+EDX analysis revealed that

![Fig. 3 Results of SEM analysis of these soils. (a) raw soils; (b) soils after adsorption.](image1)

![Fig. 4 EDX analysis images of soils after adsorption. (a) LJ; (b) TJ.](image2)
the NaOH-Pi (Fe/Al-P) was more abundant than Ca-P in acidic soils, the opposite being observed in alkaline soils. The P adsorption saturation study indicated that the major form of adsorbed P was NaOH-Pi in acidic soils, and Ca-P in alkaline soils.

The potential for P adsorption of the seven soil samples agreed with the sequence determined from the Langmuir and Freundlich models, but was a little weaker in absolute values. The results of TP removal efficiency from the dynamic column experiments indicate that it would be feasible to utilize local soil to remove P from the effluent of biological treatment systems in rural areas of China.

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