Sorption and desorption of phosphorus by shale: batch and column studies
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ABSTRACT

Constructed wetland systems have gained attention as attractive solutions for wastewater treatment. Wetlands are not efficient to treat wastewater with high concentrations of phosphorus (P). In order to remove high soluble P loads by wetland, sorbent beds can be added prior to the discharge of wastewater into wetlands. Sorption by sorbent materials is identified as a method for trapping excess P in wastewaters. In the present investigation, shale has been identified as a sorbent material for removal of phosphate (PO₄-P) due to the cost effectiveness, stability and possibility of regeneration. The study focuses on the removal of PO₄-P from wastewater using shale and the feasibility of using the P-sorbed material as slow-release fertilizer. Phosphorus sorption experiments were conducted by using shale (2 mm and 2–4.7 mm). Results indicate that Shale I (particle size = 2 mm) showed the highest sorption of PO₄-P (500 ± 44 mg kg⁻¹). Breakthrough point was reached within 10 h in columns with flow rates of 2 and 3 ml min⁻¹. Lower flow rate of 1 ml min⁻¹ showed an average residence time of about 2 h while columns with a higher flow rate of 3 ml min⁻¹ showed a residence time of about 40 minutes. Variation in flow rate did not influence the desorption process. Since very low concentrations of PO₄-P are released, Shale saturated with PO₄-P may be used as a slow nutrient release source of P or as a soil amendment. The sorbent can also be regenerated by removing the sorbed PO₄-P by using 0.1 N HCl.

Key words | desorption, phosphorus, shale, sorption

INTRODUCTION

North Carolina ranks second in swine production in U.S.A. and thereby generating million tons of manure and may cause environmental and societal problems that are related to odor, nutrients, and pathogens. Traditionally, swine operations contain flushing system in the swine houses, where the waste is flushed into an anaerobic lagoon and sprayed on agricultural fields. In many areas where swine operations are concentrated, the repeated spraying of wastewater on to fields results in P saturation which in turn may lead to eutrophication. Many studies have used constructed wetlands as P sinks for agricultural runoff (Lu et al. 2006), animal wastewater (Cronk 1996), aquaculture wastewater (Comeau et al. 2001) and agricultural wastewater (Sun et al. 2003). Constructed wetlands proved to remove 40 to 45% P from swine wastewater (Reddy et al. 2001; Poach et al. 2004) and the removal efficiency will be reduced with the age of wetlands. If the P concentration in wastewater has to be reduced further, the effluents can be treated with a P sorbing material prior to discharge into wetlands.

Filter materials used for P removal from wastewater are characterized by a high affinity for P and these reactive materials are referred to as adsorbents or sorbents. They specifically interact with the targeted species, the phosphate ions (Cucarella & Renman 2009). Minerals with reactive Fe, Al–hydroxide or oxide groups on their surfaces or
Materials and Methods

Materials

The PO₄⁻P solutions used in the P sorption experiments were prepared from analytical grade KH₂PO₄ (Fisher Scientific, Swanee, GA). All solutions and dilutions were made in deionized water.

Expanded shale of varied mesh sizes were procured from Utelite Corporation (Coalville, UT). Their physical properties (data from Utelite Corporation) are shown in Tables 1 and 2.

Batch experiments

P sorption

Lab-scale batch experiments were performed to screen substrates of better P sorption and to determine P sorption capacity of shale. The batch experiments data will be extrapolated to calculate the substrate amount, wastewater flow and retention time in real-time situation for wetlands. One gram of shale was equilibrated with 10 mL PO₄ solution in 50 ml centrifuge tubes. Solutions of varied P concentrations (C) ranging from 0 – 100 mg P L⁻¹ were prepared from KH₂PO₄. In earlier studies, different matrices like CaCl₂ (Drizo et al. 1999), KCl (Leader et al. 2008) and water (Babatunde et al. 2008) have been used. In the present investigation, the solutions were prepared in deionized water, since in the application studies wastewater rich in P would be used. The P solutions- shale mixtures were continuously stirred on a horizontal shaker (Eberbach Corporation Cat.No. 5850) for 24 h at constant room temperature. The equilibration time of 24 h was chosen based on preliminary studies and earlier studies by Drizo et al. (1999). After 24 h of equilibration, the samples were centrifuged for 10 min at 5,000 rpm and the supernatant was filtered through 0.45 μ filters and the PO₄⁻P concentrations of the samples were analyzed by Lachat Flow Injection Analyzer/Ion Chromatograph (QuikChem IC/FIA—8000 Series). This is an automated calorimetric method (EPA 365.3) of phosphate analysis where the orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex which is reduced by ascorbic acid to form a blue complex, which absorbs light at 660 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

The sorption experiments were conducted in triplicates. The amount of P sorbed (S) was calculated as the difference between the amount of PO₄⁻P in original concentration and
the amount remaining in solution.

\[ S = (C_0 - C)V/m \]  

(1)

Where, \( C_0 \) is the initial concentration (mg L\(^{-1} \)), \( C \) is the final concentration (mg L\(^{-1} \)), \( V \) is the solution volume (l) and \( m \) is the sorbent mass (g).

**Phosphate sorption maximum measurement: sorption isotherms**

Data obtained from the batch experiments expressed as PO\(_4\)-P sorbed (\( S \)) and the equilibrium solution concentrations (\( c \)) ranging from 0 to 100 mg L\(^{-1} \) were fitted to both Freundlich and Langmuir sorption isotherm equations. The Freundlich equation is represented as follows:

\[ X = Kc^{1/n} \]  

(2)

where \( K \) and \( n \) are constants. The constant \( K \) may be considered as a hypothetical index of P sorbed from a solution having a unit equilibrium P concentration, and may thus be taken to provide a measure of relative P sorption capacity of the sorbent used.

The linear form of the above Equation (1) can be written as

\[ \log X = \log K + \frac{1}{n} \log c \]  

(3)

The Equation (3) gives a linear test plot with \( \log K \) as intercept and \( 1/n \) as the slope of the equation.

The Langmuir equation can be written as

\[ \frac{c}{X} = \frac{1}{K_1K_2} + \frac{c}{K_1} \]  

(4)

where \( K_1 \) and \( K_2 \) are constants. \( K_1 \) is designated as the Langmuir sorption maximum and \( K_2 \) is related to binding energy. The Langmuir equation maximum is calculated from the slope obtained by plotting \( c \) against \( c/X \) (S) (Sakadevan & Bavor 1998).

**Continuous flow test**

A fixed bed continuous flow experiment was conducted in order to examine the uptake of PO\(_4\)-P by shale I using three different flow rates of 1, 2 and 3 mL per minute. A glass column of 2.5 cm inner diameter and 50 cm height was filled with shale and fed a solution prepared from KH\(_2\)PO\(_4\) with a concentration of 100 mg P L\(^{-1} \). Even though the swine wastewater may have other organic forms of P, based on the analysis of the wastewater, more than 80% of the total phosphorus is in the form of orthophosphate. Hence KH\(_2\)PO\(_4\) solution was used in the lab-scale studies. The feed solution was applied using peristaltic pump with a constant flow rate (Watson & Marlow, Model 323S). The feed solution concentration was chosen based on preliminary investigation on swine effluent. On pilot scale studies, the swine effluent would be subjected to solid-liquid separation using PAM (Vanotti et al. 2002), prior to removal of PO\(_4\)-P by the sorbents. The effluent after solids separation had a concentration ranging from 75–100 mg L\(^{-1} \) of PO\(_4\)-P.
Hence in the present investigation, column studies were conducted with $100 \pm 5 \text{ mg L}^{-1}$ of PO$_4$-P. Based on the previous batch studies, Shale I was chosen as the sorbent. The outlet samples after passing through the column were collected manually at specific time-intervals. The operational conditions of the column experiment are shown in Table 3 and the experimental set up is shown in Figure 1.

### Determination of breakthrough point

Breakthrough point is defined as the point where the exit concentration reaches an upper limit, which is a portion (10%) of the inlet concentration (Inglezakis 2005). In the present study, the time taken for the saturation of the sorbent material at the breakpoint was determined.

### Determination of average residence time

The average residence time in (h), $T_{\text{rave}}$ was calculated from the following Equation (Babatunde et al. 2008).

$$T_{\text{rave}} = \pi r^2 h/e Q_{\text{ave}}$$  

Where, $Q_{\text{ave}}$ is the average computed flow rate (cm$^3$ h$^{-1}$); $r$, the radius of the column (cm); $h$, the combined height of the material in the column (cm) and $e$ is the bed porosity.

Bed porosity ($e$) was determined from the bulk density ($B_d$) and particle density ($P_d$) of the material (Pushnov 2006).

$$e = 1 - (B_d/P_d)$$

### Desorption of sorbed P from bed column

The desorption of the PO$_4$-P sorbed onto the shale column, was evaluated using DI water. After saturation with PO$_4$-P, the column was flushed continuously with DI water for about 30 h. Samples were collected periodically and analyzed for PO$_4$-P using FIA. After washing the column with DI water, the column material was washed with 0.1 N HCl to investigate desorption efficiency and possible column regeneration.

### RESULTS AND DISCUSSION

#### Batch experiments

**P sorption**

The sorption of PO$_4$-P onto shale I and II increased with increasing concentration of PO$_4$-P in solution (Figure 2). It was observed that Shale I showed the maximum sorption of PO$_4$-P of $500 \pm 44 \text{ mg kg}^{-1}$, with an initial PO$_4$-P concentration of 100 mg P L$^{-1}$. However, the adsorption increases with an increase in initial concentration greater than 100 mg L$^{-1}$. Both Shale I and Shale II showed significant ($R^2 = 0.989$ and 0.95) sorption of PO$_4$-P. Since the sorption phenomena does not follow a linear trend, the percent sorption of PO$_4$-P decreased with increasing concentration of PO$_4$-P in solution for both shale materials (Figure 3).
Shale II of larger particle size showed comparatively lower sorption efficiency, because of its smaller surface area (Zhu et al. 1997) and high hydraulic conductivity than smaller particle sized material. If shale or other sorbent materials are used for wastewater treatment there could be a competition between multivalent cations for the sorption sites and may promote P sorption differences in wetlands (Novak & Watts 2006).

Phosphate sorption maximum measurement: sorption isotherms

Langmuir and Freundlich sorption isotherms were plotted from the batch experiment data. The coefficients of the isotherms are presented in Table 4. Based on the results, the value of $K$ was observed to be 69.68 and $1/n$ is 0.5747 for Freundlich isotherm in the case of Shale I. Since the value of the constant $1/n$ (adsorption intensity) is less than unity, it indicates a favorable sorption. Similar observations have been reported by Ghorai & Pant (2004) on fluoride adsorption by activated alumina. In general, the Freundlich equation modeled the P sorption data better than the Langmuir equation as observed by Sakadevan & Bavor (1998). Even though the Freundlich $K$ values give a measure of relative P adsorption capacity (a higher $K$ values equates to greater P adsorption capacity), these values are not directly related to the P adsorption maxima in the Langmuir equation. This may be because the Freundlich equation, although empirical, implies that the affinity of adsorption decreases exponentially with increasing saturation, which may be closer to reality than the assumption of constant binding energy inherent in the Langmuir Equation (Kuo & McNeal 1984). Earlier studies (Arias et al. 2001; Drizo et al. 2002; Bubba et al. 2003; Ádám et al. 2007) on estimation of P-sorption capacities of different substrates using the Langmuir-isotherm plots have shown that the maximum apparent P-sorption capacities did not correspond or correlate with the actual amount of P removed in the columns. Similarly our observations also indicate that Langmuir adsorption maxima values did not correspond to the actual P sorption, which may be attributed to other factors like calcium-phosphate precipitation (Kaasik et al. 2008), indicating that adsorption may not be the only process in the removal of P by shale.

Continuous flow test

Determination of breakthrough point

Even though the operating capacity is theoretically independent of the flow rate, it is found to be flow-rate-dependent and different from that measured in batch.
systems (Inglezakis et al. 2002; Inglezakis 2005). Typical breakthrough curves are shown in Figure 4. Error bars indicate the standard deviation of triplicates. Observations indicate that with flow rates of 2 and 3 mL min\(^{-1}\), the breakthrough point was reached within 10 h. A lower flow rate of 1 mL min\(^{-1}\) took a longer time for saturation.

**Determination of average residence time**

The average residence time of the solution in the column with Shale I was calculated based on the average computed flow rate (cm\(^3\) h\(^{-1}\)); \(r\), the radius of the column (cm); \(h\), the combined height of the material in the column (cm) and \(\varepsilon\), the bed porosity. The bed porosity was determined to be 0.98% based on a bulk density of 0.8 g/cm\(^3\) and particle density of 2.55 g/cm\(^3\). Lower flow rate of 1 mL min\(^{-1}\) (60 cm\(^3\) h\(^{-1}\)), showed an average residence time of 2 h 5 mins while columns with a higher flow rate of 3 mL min\(^{-1}\) (180 cm\(^3\) h\(^{-1}\)) showed a residence time of 42 mins (see Table 5). Observations indicate that with an increase in hydraulic loading, the residence time would obviously begin to decline resulting in a decline in removal efficiency.

Conversely, lower flow rates result in high residence times in the column and hence the removal efficiency is favored by lower volumetric flow rates (Stylianou et al. 2007; Babatunde et al. 2008).

**Desorption of sorbed P in the column**

In order to determine the possibility of recovery of the sorbed P from the sorbent, columns saturated with the sorbed P were washed with DI water at the same flow rates as were used in the column saturation experiments. The results are shown in Figure 5.

Observations indicate that the variation in flow rate did not influence the desorption process and very low concentrations of P were desorbed from the column. Since very

![Figure 4](https://iwaponline.com/wst/article-pdf/61/3/599/447961/599.pdf)

**Figure 4** | Breakthrough curves of PO\(_4\)-P sorption using Shale I showing polynomial trendlines and their associated \(R^2\) values.

**Table 5** | Average residence time of the sorbate (P) in the column at various flow rates

<table>
<thead>
<tr>
<th>Flow rate (cm(^3) h(^{-1}))</th>
<th>Average residence time (h’ mins”)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2’ 5”</td>
</tr>
<tr>
<td>120</td>
<td>1’ 3”</td>
</tr>
<tr>
<td>180</td>
<td>42”</td>
</tr>
</tbody>
</table>

![Figure 5](https://iwaponline.com/wst/article-pdf/61/3/599/447961/599.pdf)

**Figure 5** | Desorption of phosphate-P using DI water showing the moving-average trendlines.

![Figure 6](https://iwaponline.com/wst/article-pdf/61/3/599/447961/599.pdf)

**Figure 6** | Desorption of phosphate-P using 0.1 N HCl showing polynomial trendlines and their associated \(R^2\) values.
low concentrations of P are released, Shale saturated with P may be used as a slow nutrient release source in soil amendment. The possibility of regeneration of the column material was investigated by flushing out the column with 0.1 N HCl and the results are shown in Figure 6. After 33 h of desorption of the column with 0.1 N HCl, the concentration of P in the filtrate was observed to be 24 ± 2 mg L⁻¹ and 21 ± 1.3 mg L⁻¹ in columns with a flow rate of 1 mL min⁻¹ and 3 mL min⁻¹ respectively. Thus the P sorbed is released gradually and the variation in flow rate did not have a major influence on desorption of the sorbed P.

**CONCLUSION**

Experimental observations suggest that Shale can be used as a sorbent for the removal of PO₄-P from wastewater. The effluent treated porous materials can be either used as a source of nutrients that can be spread onto the farm or as soil amendment. Piggy farm effluents contain a large reserve of plant nutrients (Bolan et al. 2004) and hence these nutrients can be trapped and reused effectively. The sorbent can also be regenerated by removing the sorbed PO₄-P by using 0.1 N HCl. This investigation was carried out as a preliminary investigation to identify the sorbents for the removal of P for application in swine wastewater treatment, as a preamble step in removal of nutrients prior to treatment by constructed wetland.

**REFERENCES**


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