Magnetite for phosphorus removal in low concentration phosphorus-contained water body

Heng Xiang 1,2a, Chaoxiang Liu *,1, Ruiling Pan 2, Yun Han 2 and Jing Cao 3

1 Institute of Urban Environment, CAS, Xiamen, 361021, China
2 Key Lab of Northwest Water Resources, Environment and Ecology, MoE; Xi’an University of Architecture and Technology, Xi’an 710055, China
3 North China Institute of Science & Technology, Beijing, 101601, China

(Received October 12, 2013, Revised April 02, 2014, Accepted May 05, 2014)

Abstract. Magnetite was chosen as a typical adsorbent to study its phosphate adsorption capacity in water body with low concentration of phosphorus (below 2 mg P L⁻¹). Magnetite was collected from Luoyang City, Henan Province, China. In this research, three factors have been studied to describe the adsorption of phosphate on magnetite, which was solution concentration (concentration ranging from 0.1 to 2.5 mg P L⁻¹), suspension pH (1 to 13) and temperature (ranging from 10°C to 40°C). In addition, the modified samples had been characterized with XRD and FE-SEM image. The results show that iron ions contains in magnetite were the main factors of phosphorus removal. The behavior of phosphorus adsorption to substrates could be fitted to both Langmuir and Freundlich isothermal adsorption equations in the low concentration phosphorus water. The theoretical saturated adsorption quantity of magnetite is 0.158 mg/g. pH has great influence on the phosphorus removal of magnetite ore by adsorption. And pH of 3 can receive the best results. While temperature has little effect on it. Magnetite was greatly effective for phosphorus removal in the column experiments, which is a more practical reflection of phosphorous removal combing the adsorption isotherm model and the breakthrough curves. According to the analysis of heavy metals release, the release of heavy metals was very low, they didn’t produce the secondary pollution. The mechanism of uptake phosphate is in virtue of chemisorption between phosphate and ferric ion released by magnetite oxidation. The combined investigation of the magnetite showed that it was better substrate for water body with low concentration of phosphorus.

Keywords: magnetite; low concentration; phosphorus adsorption

1. Introduction

The water quality problems causing by phosphorus discharge in past decades have been raising many concerns worldwide, thus many countries have introduced stricter wastewater discharge standard of phosphorus. Phosphorus release sources generally include natural mineral deposits, domestic and industrial wastewater and agricultural runoff (Nesbitt 1969). Phosphorus is a limiting...
nutrient to maintain the phytoplankton and algae growing in water, and also contributes to eutrophication. It is reported that low concentration phosphorus discharged sewage (less than 1 mgL⁻¹) may cause eutrophication (Zhao and Sengupta 1998). Release of phosphorus from anthropogenic sources such as municipal wastewater, runoff from agricultural areas and landfill leachate to lakes, rivers, and coastal areas constitutes the main risk for reduced water quality and eutrophication. At the same time, $P$ is an essential nutrient for all forms of life and cannot be replaced by any other element. There are a variety of ways to remove the phosphorus in water, and the most practical methods are adsorption and precipitation of substrate, uptake of microbial and plant. Among these three methods, substrate adsorption is the main way, while the uptake of microbial and plants take a small fraction of the whole remove. Phosphorus in the water environment generally exists in three forms: organic phosphorus, polyphosphate and orthophosphate (Minton and Carlson 1972). In the biological treatment process, both organic phosphorus and polyphosphate are decomposed to orthophosphate by bacteria, and then removed by chemical precipitation. In this way, phosphate is transferred from the liquid phase to the solid phase, and requires further treatment. In addition, this process is affected by pH, total alkalinity and ion concentration. Therefore both biological chemical phosphorus removal have their shortages (Ensar 2005, Zha and Jordan 2010, Qiu et al. 2010). Iron and aluminum oxides, activated alumina, red mud and other adsorbents have been mentioned in some reports (Akay et al. 1998, Ayoub et al. 2001, Brattebo and Ødegaard 1986), but the phosphorus adsorption capacities of these materials are still limited.

Magnetite is a kind of oxide mineral with the main component of Fe₂O₄. The microhardness of magnetite ore ranges from 515 to 550 kg mm⁻², with an average of 528 kg mm⁻². While its density is in the range of 5.16 to 5.18 g cm⁻³. The magnetite ore has strong magnetic, brittle, odorless and tasteless. Magnetite is broadly distributed in nature, and it could remove low concentrations phosphorus from wastewater by adsorption. Magnetite could continue to release iron slowly in the environment. This feature will be potential to remove phosphorus as the adsorbent. To the author’s knowledge, phosphorus adsorption by magnetite has not been reported at home and abroad. Therefore, this study is to assess the availability of magnetite remove low concentration phosphorus from wastewater.

2. Materials and methods

2.1 Materials

The Magnetite was purchased from Luoyang, Henan Province. Before the experiment, the material was broken to small pieces, screening diameter in 5-10 mm, then drying and saving. Sieving particle size of 60 to 100 mesh ore powder preservation after drying.

2.2 Physicochemical properties

The porosity of magnetite was determined using the standard soil science procedure, based on the estimations of bulk density and true density (Xue et al. 2009). Surface area and pore size analyzer (ASAP2020M+C) is used to measure the surface area and pore size of the fillers. Using the field-emission scanning electron microscope (FE-SEM) observes the surface of fillers and its chemical component, combine further with XRD to confirm the fillers’ chemical component.
2.3 Phosphorus adsorption

2.3.1 Batch test

Seven different phosphorus solutions (the volume of each solution was 100 mL), concentration ranging from 0.1 to 2.5 mg P L\(^{-1}\) (Ayoub et al. 2001), were equilibrated with 1 g of magnetite for 48 h by continuous shaking in a rotating shaker (150 rpm) at constant temperature (25°C). Three drops of chloroform were added to each erlenmeyer flask to inhibit microbial activity. Seven solutions with different pH values (the volume of each solution was 100 mL, 0.5 mg PL\(^{-1}\)), ranging from 1 to 13, and seven solutions with different temperature (the volume of each solution was 100 mL, 0.5 mg PL\(^{-1}\)), ranging in temperature from 10°C to 40°C, were equilibrated with 1 g of magnetite for 48 h by the same condition. At the end of the equilibration period, an aliquot of the supernatant was filtered through a 0.45 μm filter. Based on the test, the Langmuir and Freundlich isotherm models were used to describe the adsorption equilibrium. Two parallels were used for all measurements, and the experiments were repeated three times.

2.3.2 Column test

For column experiments, 1800 g of magnetite was packed in a column (i.d.: 60 mm, height: 300 mm), and a total of 3 columns were used. The low concentration phosphorus-contained water was supplied continuously to the bottom of each column by a peristaltic pump. Total Phosphorus (TP) concentration of influent was maintained at 0.5 mg L\(^{-1}\), and flow rate was controlled at about 5 L min\(^{-1}\). The effluent of each column were measured daily to estimate phosphorus concentration until the effluent concentration of TP approached the influent concentration of TP. In order to mimic the actual operating conditions, the influent was prepared using the landscape river water with a constant TP concentration of 0.5 mg L\(^{-1}\), and the flow rate was maintained at about 5 mL min\(^{-1}\). The final effluent TP concentration was the average of the parallel tests. In order to assess the feasibility of magnetite, heavy metals contents were measured once per month by ICP-MS.

![Fig. 1 Experimental device for the column test](image-url)
3. Results and discussion

3.1 Physicochemical properties

Some physicochemical properties of magnetite are shown in Table 1, Figs. 2 and 3. It is reported that the filler’s chemical composition and forms have significant effect on its phosphorus...
Magnetite for phosphorus removal in low concentration phosphorus-contained water body

adsorption capacity, but not the physical properties (Drizo et al. 1999). However, the physical properties could have great impact on the adhesion of microbial and the growth of plants, which would further affect the phosphorus removal of the system. As shown in Fig. 2, magnetite’s surface is rough, porous, irregular, and with a high specific surface area, which are conducive to the growth of microorganisms.

Strang and Wareham (2006) have demonstrated that the chemical form of metals (such as Ca, Fe, Mg, Al, etc.) in a substrate should also be considered when selecting a potential substrate for phosphorus removal. The magnetite contains large amounts of crystalline iron oxides. Fig. 3 is the phase analysis of magnetite, which is analyzed by XRD and fitted with X’Pert HighScore Plus software. It is shown that the main ingredients in magnetite are iron oxide and silica, and a little of calcium-aluminum crystalline compound. The result is similar to the conclusion of SEM-EDX analysis. Phosphorus could form insoluble compounds with Fe$^{3+}$, Al$^{3+}$ and Ca$^{2+}$ in water, thus would be removed. Therefore, the filler’s physical and chemical properties are an important parameter for Phosphorus Removal in the constructed wetland system.

3.2 Phosphorus adsorption

3.2.1 Adsorption isotherm experiments

The result of trials indicated that the $P$ removal efficiency of the magnetite first increased and then decreased with the increasing of phosphate concentration, under the isothermal condition. The highest $P$ removal efficiency (48.48%) occurred at $P$ initial concentration of 0.5mgL$^{-1}$. The $P$ adsorption capacity of magnetite increased with the increase of $P$ concentration, but was still relatively low in the batch experiments. Some researchers have reported that the $P$ adsorption capacity was usually low in the low $P$ concentration water (Mann and Bavor 1993, Jensen et al. 1992). The result of this test also showed that the magnetite’s adsorption capacity was low in the low $P$ concentration water.

Langmuir and Freundlich models are used to describe the isothermal adsorption equilibrium. The equation of Langmuir model is

$$\frac{1}{m} = \frac{1}{X_m} + \frac{1}{K_mC}$$

Where $c$ is the concentration of PO$_4^{3-}$ in the solution at equilibrium (mg L$^{-1}$), $m$ is the amount of PO$_4^{3-}$ adsorbed per unit weight of material (mg g$^{-1}$) at equilibrium, $X_m$ is the phosphorus adsorption maximum (mg g$^{-1}$), $K_m$ is the constant related to the binding strength of phosphorus on the material.

The equation of Freundlich model is

$$\ln G = n \ln C + \ln K$$

Where $C$ is the concentration of PO$_4^{3-}$ in the solution at equilibrium (mg·L$^{-1}$), $G$ is the amount of PO$_4^{3-}$ adsorbed per unit weight of material (mg g$^{-1}$) at equilibrium, $n$ is a constant, $K$ is a constant related to the adsorption energy.

Isotherm constants and values of $R^2$ for the magnetite were shown in Table 2.

The results showed that both the Langmuir and Freundlich equation could match the experimental fillers’ properties of $P$ isotherm adsorption. According to the Langmuir equation, the magnetite’s $P$ adsorption maximum is calculated as 0.158 mg g$^{-1}$. It is an important parameter
for filler selection, which can provide initial reflection of filler’s phosphorus purification capability, and the result also indicated the magnetite’s saturated adsorption amount was low in low $P$ concentration water. But some researchers believe that the filler’s $X_m$ values will vary with the condition of static test. Therefore, there are many uncertainties when using the $X_m$ by the batch test to predict the packing life. $N$ in the Freundlich equation could reflect the $P$ adsorption strength of magnetite, and $K$ is positively correlated with the $P$ adsorption capacity. The results (Table 3) shown that magnetite could have strong adsorption of the low concentration $P$.

3.2.2 Effect of pH on magnetite

Fig. 4 represented the removal efficiency of 0.5 mg L$^{-1}$ solution by magnetite adsorption, when pH value ranging from 1 to 13. The static test indicated that magnetite only had a high $P$ removal efficiency, while pH was about 3, while it showed almost no $P$ removal when pH was 1 or above 5. Fig. 4 showed that the amount of phosphorus released by magnetite in different pH condition. The result demonstrated that when pH was above 3 the $P$ released of magnetite tended to stabilize at about 0.01 mg g$^{-1}$.

The chemical composition of magnetite is Fe$_3$O$_4$, thus it contains large amounts of divalent and trivalent iron. In nature, magnetite may continue to release Fe$^{2+}$ and Fe$^{3+}$, which can react with PO$_4^{3-}$ and form insoluble compounds to achieve the purpose of removal phosphate (Eberhardt and Min 2008).

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_m$</td>
<td>$X_m$</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.0867</td>
<td>0.158</td>
</tr>
</tbody>
</table>

Table 2 Adsorption isotherms of the magnetite and relevant parameters

Fig. 4 Effect of pH on adsorption efficiency of phosphate by magnetite
Magnetite for phosphorus removal in low concentration phosphorus-contained water body

\[
\begin{align*}
\text{Fe}^{3+} + \text{PO}_4^{3-} & \rightarrow \text{FePO}_4 \\
\text{Fe}^{2+} + \text{PO}_4^{3-} & \rightarrow \text{Fe}_2(\text{PO}_4)_2
\end{align*}
\]

However, iron ions are prone to hydrolysis in water (Byrne et al. 2000, Rose and Waite 2003)

\[
x\text{Fe}^{3+} + y\text{H}_2\text{O} \leftrightarrow \text{Fe}_x(\text{OH})_{y(3x-y)} + y\text{H}^+
\]

In the acid condition, due to the abundance of hydrogen ions, the hydrogen hydrolysis reaction could be inhibited, and FePO_4 is easily produced. When pH is below 5, Fe^{3+} could effectively combine with PO_4^{3-} to form FePO_4 precipitate. When pH is above 5, there is a competition between PO_4^{3-} and OH^-, which would reduce the P removal rate of magnetite. When pH is about 1, there are a large number of hydrogen ions in solution, which would cause part of the magnetite particles to dissolve and P release from the magnetite particles, thus increase the P content of the water. In summary, pH has a strong impact on the P absorption of magnetite, and the removal of phosphorus is highest at pH 3.

3.2.3 Effect of temperature on magnetite

Experimental results showed the phosphorus removal efficiency of magnetite at different temperatures (ranging from 10°C to 40°C) in low P concentration water. In the static test, the removal efficiencies were between 30% and 50% and the adsorption capacities were between 0.015 and 0.025 mgg^{-1}. Therefore, there is no significant effect of temperature on low P concentration adsorption.

Under the actual operating conditions, temperature and pH were important factors (Bar-Yosef et al. 1988). The above results showed that pH had large impact on phosphorus adsorption on magnetite, while the temperature had little impact, which indicates that magnetite could be a suitable filler for practical application. As southern China is in subtropical region, perennial temperature is between 0 to 40°C (Bar-Yosef et al. 1988), with obvious seasonal changes of climate. Therefore, magnetite may be favourable for applications in this area. As magnetite could be used as filler and placed underground, the temperature impact is small, promising its broad application prospects.

3.2.4 Column experiments

The breakthrough test of phosphorus adsorption on magnetite was conducted as well. Under the condition of influent concentration \( C_0 \) were kept constant and the adsorption column continuous operation, it would estimate the magnetite’s adsorption capacity of phosphorus removal, by examining the effluent phosphorus concentration \( C_t \) (or the treated water volume) changes with time. The breakthrough curve was based and developed on this. It could describe the the effluent and influent phosphorus concentration ratio \( C_t/C_0 \) (or treated water) changes with time, during the adsorption column long-time operation. Isotherm adsorption model could reflect the phosphorus removal capabilities of magnetite, but it could not accurately evaluate the adsorption capacity (Sakadevan and Bavor 1998). Conditions of batch test differ greatly with actual operating. Hence, it is necessary to study the dynamic P adsorption of magnetite. The results of magnetite adsorption column for phosphorus removal are shown in Fig. 5.
According to the data (Figs. 4 and 5), the removal efficiency of magnetite is higher when pH was between 2 to 4. During the first 115 days of the test, the \( P \) removal efficiency was above 60%, and the effluent concentration of \( P \) was below 0.2 mg L\(^{-1}\). After 115 days of operation, the penetration started, and full penetration was observed at the 150th day with the effluent concentration increased from 0.2 mg L\(^{-1}\) to 0.5 mg L\(^{-1}\). During the test, the \( P \) retention capacity of magnetite was about 250 mg, indicating a adsorption capacity of 0.139 mg g\(^{-1}\), which was lower than the maximum adsorption capacity fitted by the Langmuir equation.

The breakthrough curve could be divided into three parts in Fig. 5. During the initial operating stage of adsorption column, the magnetite had more surface active absorption sites, and the adsorption capacities were stronger, so the effluent phosphorus concentration and the \( C_t/C_0 \) value were low. Running for a period of time, the magnetite adsorption capacity of phosphorus would decreases gradually, with the surface active absorption sites decreasing. These were presented as the effluent phosphorus concentration and the \( C_t/C_0 \) value increasing continuously. But the effluent phosphorus concentration was still lower than the influent in this stage. At the later running period, the magnetite basically reached adsorption saturation state, the effluent phosphorus concentration would tend to the influent, and \( C_t/C_0 \rightarrow 1 \). Generally, when the \( C_t/C_0 \) value was 0.95, the adsorption column was breakthrough and lost the capacity of adsorption.

### Table 3 The release amount of some elements in magnetite

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2144</td>
<td>2.332</td>
<td>60.07</td>
<td>1.158</td>
<td>0</td>
<td>4.879</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.6195</td>
<td>51.9</td>
<td>74.62</td>
<td>1.973</td>
<td>0</td>
<td>9.776</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.1881</td>
<td>721.6</td>
<td>142.8</td>
<td>2.88</td>
<td>0</td>
<td>13.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>10.69</td>
<td>100.5</td>
<td>109.7</td>
<td>5.101</td>
<td>0</td>
<td>19.72</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Unit: ppb
In the recent reports, the study were increasing gradually, which using the breakthrough curves investigate the adsorption capacity of fillers for phosphorus removal, for example, Ugurlu and Salman (1998), Wang et al. (2013), Karaca et al. (2006), Dunne et al. (2005), and Brooks et al. (2000). They studied the adsorption breakthrough on ash, oyster shells, wetland soils Phosphate adsorption and wollastonite, respectively, and also estimated their abilities of phosphorus removal. Obviously, it would be more approach to the practical operation, using the method that combine the adsorption isotherm model with the breakthrough curves.

The results in Table 3 showed that the concentration of heavy metals in effluent and the pH value is between 6 to 7, which were all lower than the type II water quality standard of “Surface Water Environmental Quality Standard” (GB 3838-2002) in China. Therefore, the large-scale application will not bring new hazards to the environment (Wan Ngah and Hanafiah 2008, Ismail and Aris 2013).

4. Conclusions

After a series of adsorption tests, the results showed that:

1. At 25°C, both Langmuir and Freundlich equation can reasonably describe the adsorption, and the maximum adsorption capacity fitted by Langmuir equation was 0.158 mg g⁻¹.

2. The results showed that pH had a great impact on the P removal on magnetite. P removal efficiency was highest at pH 3. Temperature had no significant impact on P removal efficiency for low P concentration water.

3. Column tests showed that the P removal efficiency by magnetite was highest for low P concentration water at pH about 3. Before penetration, the removal rate could be more than 60%. The concentrations of heavy metals in the effluent were very low, thus the application of magnetite in phosphorus removal would not bring new hazards to the environment.

4. Magnetite could continuously release Fe³⁺, which could be combined with phosphorus Fe³⁺ and formed insoluble compounds in the water body. Thus, it could achieve the phosphorus removal.

Acknowledgments

This research was supported by National Major Project on Water Pollution Control and Management Technology of P.R. China (2012ZX07302-002).

References

Heng Xiang, Chaoxiang Liu, Ruiling Pan, Yun Han and Jing Cao

20(8), 977-986.


CC