Semi-continuous Magnetic Removal of Phosphate Using an Iron Oxide Hydroxide Adsorbent and Regeneration of Its Adsorbent

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Phosphate removal from wastewater using fine-particles of schwertmannite was performed by use of a semi-continuous magnetic filtration. The effects of two main parameters of magnetization and drag forces on the performance of the magnetic filtration were investigated. By increasing the magnetic intensity from 0.4 to 4 T, the magnetic filter performance was increased from less than 0.7 up to 0.99 depending on the fluid velocity through the magnetic filter. The measured results in magnetic filtration tests were in consistency with the theoretical results applied in this study. It was revealed that the schwertmannite possessed a high regeneration ability with trivial loss of adsorption capacity. Moreover, the phosphate adsorption capacity in schwertmannite was remarkably increased by using an acid-modification method.

KEY WORDS: magnetic filter; phosphate removal; schwertmannite; wastewater; electromagnetic processing of materials; regeneration.

1. Introduction

The magnetic filtration (MF) using low-cost adsorbents and supplement materials has become a promising technology in wastewater treatment due to its simplicity and rapid solid–liquid separation. Schwertmannite with the ideal formula of $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ as a chemical adsorbent can be easily separated from its aqueous medium through a magnetic filter under a relatively low magnetic intensity of around 1 T without magnetic seeding.¹⁾ Furthermore, it is a highly reactive nanoscale crystalline material with high adsorption capacity,²⁾ high solubility and high metastability^{3,4)} and can be precipitated from acid sulfate aqueous solution in pH range from 2.3 to 3.6 under oxidizing and SO_4 -rich conditions. Due to the high specific surface area and reactivity, the schwertmannite plays an important role in the adsorption or incorporation of mobilizing elements in surface and ground water systems, such as soils and mine tailings impoundments. Also, it has been reported that the schwertmannite can successfully remove arsenate and phosphate from aqueous solutions.^{1,6)} Although most adsorbents made of metal oxide require acidic conditions for phosphate removal, the schwertmannite can effectively adsorb phosphate under neutral pH condition.¹⁾ The excess SO_4^{2-} adsorbed onto the surface sites of the schwertmannite exchanges with singly coordinated surface groups⁷⁾ and sulfate ions are bound to the schwertmannite, both into the structure (tunnel sulfate) and the surface in a ratio of about 3 : 1.⁸⁾ Accordingly, the artificial modification of the schwertmannite structure by raising surface-sulfate ions could

result in the enhancement of adsorption capacity.

The present work has been focused on (i) the activation of the schwertmannite using an acid-treating process, (ii) regeneration and reusing possibility of the schwertmannite and (iii) utilizing a semi-continuous high magnetic filtration process.

2. Experimental

A model wastewater, which contained phosphorous in the form of phosphate ions, was prepared by dissolving a known amount of KH_2PO_4 in dionized water. The schwertmannite was produced by homogenous hydrolysis of iron ferric salt ($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$) using urea as a neutralizing agent.^{1,9)} The schwertmannite powder was chemically activated by using 0.05 M sulfuric acid in pH ~ 1.5 where 5 g of the dried schwertmannite was subjected to 200 cc of the diluted acid and well mixed for 30 min at room temperature. Then the filtered sample was washed with distilled water for 3–5 times to remove free surplus sulfate ions till reaching to the neutral pH and finally dried at the temperature less than 40°C. The same procedure as described above was performed for regenerating the saturated schwertmannite using 0.05 M sulfuric acid. Three cycles of regeneration were conducted under the same experimental conditions. The non-activated, activated and regenerated schwertmannites were used as the phosphate adsorbent in batch experiments. 50 ml of the solution with desired concentrations of P and the adsorbent were mixed in a bottle of 100 mL and shaken for about 3 h to reach to the equilibrium state.

Fig. 1. A schematic view of semi-continuous magnetic filtration set-up.

Then the yielded solution was filtered through a paper filter and then phosphorous concentration in filtrate was analyzed.

Figure 1 shows a schematic view of the semi-continuous experimental set-up for magnetic filtration. A magnetic filter which consisted of a ferromagnetic wire-matrix was laid at the place with the highest gradient of magnetic field in a magnet. A slurry with the schwertmannite concentration of about 173 mg/L was mixed into a distilled water and stirred for 24 h. Then, by using an adjustable pump, the slurry was passed upward through the matrix of the magnetic filter, with cylindrical shape of 6 cm (length) and 2 cm (diameter), under various fluid velocities of 0.13–0.3 m/s and magnetic intensities from 0.4 to 4 T. It is noticed that in order to stabilize the fluid flow passing through the magnetic matrix of the filter, the upward flow model, which has mostly been used in many pervious works, has been applied in our experimental set up. The effluent of the magnetic filter was gathered and dissolved into a diluted sulfuric acid, and then Fe concentration was measured by using an inductively coupled plasma atomic emission spectroscopy (ICP). The concentrations of phosphorous and sulfate ions in the filtrate were measured by using a mobile laboratory photometer, LASA 30, with the specified measuring filters of 800 and 440 nm, respectively. The particle size distribution and the mean size of the schwertmannite particles were determined using a laser scattering particle size distribution analyzer (LA-920) and the diameter of the ferromagnetic wires used as the matrix in the magnetic filter was measured by using a SEM apparatus.

3. Results and Discussion

3.1. Adsorption Capacity

In order to compare the adsorption capacity of the activated schwertmannite with the non-activated schwertmannite, the Langmuir isotherm, which was well fitted with the schwertmannite adsorption data in the pervious work,¹⁾ was applied. The Langmuir isotherm that is derived under the assumption of a monolayer adsorption with a constant ad-

Fig. 2. Amount of sorbate at equilibrium in varying initial P concentration.

Fig. 3. Langmuir plots of P adsorption at adsorbent concentration of 1 g/L for activated and non-activated schwertmannite.

sorption energy and the dimensionless adsorbate amount q_e can be obtained from Eqs. (1) and (2).

$$q_e = \frac{QbC_e}{1 + bC_e} \quad \text{.....(1)}$$

$$\frac{C_e}{q_e} = \frac{1}{bQ} + \frac{C_e}{Q} \quad \text{.....(2)}$$

where q_e is the surface concentration (mg adsorbate/g adsorbent), Q and b the Langmuir isotherm constants, C_e the P concentration in the solution at equilibrium. The isotherm constants, Q and b were estimated by fitting a set of experimental data to the isotherm model given in Eqs. (1) and (2). Figure 2 shows the experimental results of phosphorous adsorption onto the non-activated and activated schwertmannites of 1 g/L at different initial P concentrations from 20 to 100 mg/L. The adsorption amount of P on the activated schwertmannite was significantly increased by increasing the initial P concentration. At the same initial P concentrations, the activated schwertmannite adsorbed more amount of P than non-activated one. To find out the adsorption capacity and ascertain the adsorption isotherm compatibility, the Langmuir plots for P adsorption on the both adsorbents were depicted as shown in Fig. 3. For the maximum initial P concentration of 100 mg/L, the P adsorption capacities Q of both the adsorbents were determined from the slope of the Langmuir plots as 32.7 and 44.2 mg/g, respectively. It is noticed that the activated schwertmannite demonstrated much higher P-adsorption

Table 1. Comparing P adsorption capacity in various P-adsorbents.

Chemical adsorbent	Adsorption capacity mg/g	
	P	PO ₄
Furnace slag	0.65	2.0
Fe/Cr hydroxide	2.1	6.4
Iron oxide-coated quartz	2.6	8.0
Hematite	3.0	9.2
Al oxide-coated quartz	4.2	13
Palygorskite	8.3	25.5
Fly ash	14	43
Non-activated schwertmannite	33	100
Activated schwertmannite	44	136

Fig. 4. Amount of exchanged sulfate ions versus adsorbed P.

capability in comparison with the non-activated one. The comparison of adsorption capacity with some other P-adsorbents^{10–15)} is given in **Table 1**, where the activated schwertmannite appears as a strong P-adsorbent in comparison with the other adsorbents.

To verify the role of the activation process and ascertain to what extent the surface sulfate ions can affect the phosphate adsorption, the amount of the released sulfate ion in the filtrate after treatment using both the adsorbents was measured as a function of q_e as shown in **Fig. 4**, where the initial P concentrations were set at 40, 60, 80 and 100 mg/L. The amount of the consumed adsorbent was also determined under 1 g/L in a contact time of 3 h. Figure 4 apparently indicates that the value of q_e is proportional to the amount of the released sulfate ions in the filtrate. It is easy to show that by increasing the amount of sulfate ions in the acid-activation process, the value of q_e was fairly increased. It is furthermore clear that P-adsorption is mainly attributed to the ion-exchange mechanism in this process. In the case

Table 2. Comparison of P adsorption efficiency between the non-activated schwertmannite, and the reused and activated schwertmannite.

Adsorbent	Activated schwertmannite			Non-activated schwertmannite
	1	2	3	
Cycle number	1	2	3	1
P-adsorption efficiency %	99.7	96.9	94.5	80

of the non-activated schwertmannite, the concentrations of sulfate ions in the filtrate were varied from 13 to 11 mg/L for q_e values of 32 to 25 mg/L, while in the case of the activated schwertmannite, the sulfate ion concentration was obtained to be 20 to 15 mg/L for q_e values of 45 to 34 mg/L. Consequently, the ratio of q_e/SO_4 was obtained as 3.7 and 2.3 for the non-activated and activated schwertmannites, respectively.

3.2. Regeneration of Adsorbent

Table 2 shows the P-adsorption efficiency corresponding to the first, second and third cycles of using the activated and regenerated schwertmannite in comparison with the non-activated schwertmannite. The P-adsorption efficiency ζ was identified as the following equation;

$$\zeta = \frac{c_0 - c_e}{c_0} \times 100 \quad \text{.....(3)}$$

where c_0 and c_e are the initial and equilibrium P concentrations, respectively. The initial P-concentration and the amount of the adsorbent were set to be 20 mg/L and 1 g/L, respectively. The pH value of the solutions in all batch tests was kept around 6.8. The activated schwertmannite was successfully recycled for the three times with less than 6% total loss in adsorption capacity. The P adsorption capacity of the regenerated-activated schwertmannite for all the three cycles was higher than that of the non-activated schwertmannite. The reason for this achievement can be explained by the positive influence of the activation process which is accompanied to assist the regenerated adsorbent to be more effectiveness. That is, in each batch of the regeneration, by increasing the amount of the exchangeable sulfate ions on the surface structure of the schwertmannite, the adsorption capacity is improved itself.

3.3. Magnetic Filter Performance

Magnetic filtration was found as an efficient method for the separation of schwertmannite fine particles suspended in a liquid.¹⁾ To obtain the main practical parameters relating to the magnetic filtration and evaluate the performance of the filter in this process, semi-continuous experiment as schematically shown in Fig. 1 was carried out for different fluid velocities and magnetic intensities. Then the results were compared with theoretical values computed under some reliable assumptions. Most commonly used models to explain particle capture in a magnetic filter have been mainly borrowed from the theoretical description of deep-

bed filtration, DBF.¹⁶⁾ In a magnetic filter with randomly packed-ferromagnetic wires, magnetization and drag forces are assumed as the main forces acting on a paramagnetic particle passing through the filter, but the effect of the gravity and Archimedes forces are neglected due to fine size particles.¹⁷⁻²⁷⁾ The main force in the magnetic separation is the magnetization force which is expressed as;

$$F_m = \frac{1}{2} \frac{\chi V_p \nabla(B \cdot B)}{\mu_0} \quad \text{.....(4)}$$

where F_m is the magnetic force, V_p the particle volume, χ the magnetic susceptibility of particles, μ_0 the magnetic permeability of the vacuum and B the magnetic flux density. Also, a viscous drag force acts on the particle moving under a magnetic field in the opposite direction, which is given by the Stokes equation as shown in Eq. (5).

$$\begin{aligned} F_v &= -6\pi\eta R(\vec{v}_p - \vec{v}_f) \\ &= -6\pi\eta RV \quad \text{.....(5)} \end{aligned}$$

where η is the liquid viscosity, $\vec{v}_f$ and $\vec{v}_p$ the velocities of the liquid and particle, respectively and R the particle radius. By assuming that the liquid flow is laminar with a uniform velocity of V_m and low particle concentration, and the gradient of the magnetic flux density ∇B in the vicinity of the magnetically saturated ferromagnetic wires in the matrix of the magnetic filter is $M_s \mu_0 / a$, the ratio of F_m to F_v can be written as;

$$\frac{F_m}{F_v} = \frac{2\chi M_s B R^2}{9\eta V_m a} \quad \text{.....(6)}$$

where M_s is the saturation magnetization of ferromagnetic wires with radius a . The characteristic velocity, so-called magnetic velocity, V_m can be obtained from the balance of the magnetization and drag forces acting on the particle, i.e., $F_m/F_v = 1$.

$$V_m = \frac{2\chi M_s B R^2}{9\eta a} \quad \text{.....(7)}$$

The magnetic filter performance ξ can be calculated by taking account of the ratio of the number of escaping particles N_{out} to the number of particles entering into a filter N_{in} as;

$$\xi = 1 - \frac{N_{out}}{N_{in}} \quad \text{.....(8)}$$

Considering f as the packing fraction of ferromagnetic wires located in a matrix, the ratio of escaping particles to particles entering in a magnetic filter may be obtained by the following equation.^{18,25)}

$$\frac{N_{out}}{N_{in}} = \exp\left(-\frac{4}{\pi} f L_a^{0.5}\right) \quad \text{.....(9)}$$

where L_a is the normalized filter length defined as below.

$$L_a = \frac{V_m}{V} \frac{L}{a} \quad \text{.....(10)}$$

where L is the length of a filter.

By substituting Eqs. (7) and (10) into Eq. (9) and taking logarithm of both the sides of Eq. (9), the following equation representing a relation among the ratios of the leaving and entering particles in a filter, and the two items of magnetic flux density and fluid velocity can be obtained;

$$\ln \frac{N_{out}}{N_{in}} = \alpha \left(\frac{B}{V_0}\right)^{1/2} \quad \text{.....(11)}$$

where α is given as below.

$$\alpha = -\left(\frac{4\sqrt{2}}{3\pi}\right) \frac{fR}{a} \sqrt{\frac{\chi M_s L}{\eta}} \quad \text{.....(12)}$$

which is considered as a constant value in this study. For the schwertmannite, the measured magnetic susceptibility was 4×10^{-4} ,¹⁾ with measured particles size ranged from 0.3 to several μm , with the mean particle radius of $8 \mu\text{m}$. As shown in Fig. 1, a ferromagnetic matrix of 6 cm length and 2 cm diameter with the packing fraction of 0.03 and saturated magnetization of ferromagnetic wires of $(0.2/4\pi) \times 10^7$ A/m was used in the magnetic filter. From those experimental conditions, the value of α given in Eq. (12) was calculated as $-55 \text{ (m/(T s))}^{1/2}$. The extraction performance for the filter under various magnetic fields from 0.4 to 4 T at three fluid velocities in the magnetic filter of 0.13, 0.2 and 0.3 m/s was plotted in Fig. 5 and compared with theoretical results computed by using Eqs. (8) and (11). Moreover, the

Fig. 5. Experimental and theoretical values of magnetic filter performance versus magnetic intensity of the magnetic filter.

inner figure in Fig. 5 illustrates the experimental and theoretical results in the relation between $\ln(N_{\text{out}}/N_{\text{in}})$ and the square root of the magnetic flux density. As being indicated by Eq. (11), both the results are nicely plotted by the linear relations. It is obviously shown that the experimental results well quantitatively agree with the theoretical ones. For each fluid velocity, the filter performance increased with increasing magnetic intensity of the filter. The filter performance yielded more than 0.9 after 1 T and indicated the effectiveness of the magnetic filtration process especially beyond 1 T and nearly whole of the particles was separated at 4 T. Furthermore, there was a significant decrease in the performance with increasing fluid velocity from 0.13 to 0.3 m/s, particularly at less than 1 T. It is also noticed that the high capability of the magnetic filtration can capture schwertmannite particles over a wide range of size from less than 0.3 μm to several μm .

4. Conclusions

Phosphate removal from wastewater using schwertmannite and magnetic filtration was studied and the following results have been obtained.

(1) By using an activation process of acid modification, P adsorption in the schwertmannite is drastically increased.

(2) Regeneration of the schwertmannite can be used for P-removal.

(3) The magnetic filtration model verified the experiments results obtained in the semi-continuous magnetic filtration.

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Nomenclature

a : Radius of matrix wire (m)
 b : Langmuir isotherm constant ($\text{L}/\text{m} \cdot \text{g}$)
 B : Magnetic flux density (T)
 C_e : Phosphate concentration at equilibrium (mg/L)
 F_m : Magnetization force (N)
 F_v : Drag force (N)
 f : Packing fraction of wire matrix (—)
 L : Matrix length of a magnetic filter (m)
 L_a : Normalized matrix length (—)
 N_{in} : Number of particles entering to a filter
 N_{out} : Number of particles escaping from a filter
 M_s : Saturated magnetization of ferromagnetic wires in

matrix (A/m)

q_e : Dimensionless adsorbate amount (adsorbate (mg)/adsorbent (g))
 Q : Maximum adsorption capacity of adsorbent (mg/g)
 R : Particle radius (m)
 V : Relative velocity between fluid and particles (m/s)
 V_f : Fluid velocity (m/s)
 V_m : Magnetic velocity (m/s)
 V_p : Particle velocity (m/s)
 χ : Magnetic susceptibility of particle (—)
 η : Liquid viscosity ($\text{N s}/\text{m}^2$)
 ζ : P adsorption efficiency (%)
 ξ : Magnetic filter performance (—)
 α : Constant coefficient ($\text{m}/(\text{T s})^{1/2}$)
 μ_0 : Magnetic permeability of vacuum (H/m)

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