Removal of high-concentration phosphate by calcite: Effect of sulfate and pH

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1. Introduction

Phosphorus has long been recognized as the most critical nutrient that limits water productivity. The wide use of phosphorus in industrial products such as fertilizers, detergents, pesticides, and water softeners, etc., produces large amounts of phosphorus-bearing wastewater. Especially in the manufacture of paints, the phosphate concentration of wastewater from the degreasing, phosphating, and painting departments can reach thousands of mg/L coexisting with numerous cations and anions (such as Mg2+, Ca2+, CO3 2−, SO4 2−, etc.) in a wide pH range. The sulfate concentration sometimes approaches its saturation level. Before wastewater is discharged into water bodies, removing phosphate is usually obligatory [1]. Many technologies have been applied to remove phosphate from wastewater, including precipitation of phosphate by metal salts, cultivation of microorganisms in wastewater, constructed wetlands, and enhanced biological phosphorus removal (EBPR) [1].

Research has proven that phosphate can be effectively removed by calcite [2–8]. The reaction mechanisms of phosphate with calcite further reveal that phosphate can be either adsorbed by calcite at a low concentration, typically <20 μmol/L [4,9], or precipitated at a high concentration [4–11]. Detailed studies have been conducted on the adsorption of phosphate by calcite at low phosphate concentrations [3,12]. The adsorption of phosphate by calcite can be described by Langmuir adsorption isotherms, probably due to monolayer adsorption. Kuo et al. reported that about 80% of phosphate anions were adsorbed within 10 s, possibly because phosphate ions replaced adsorbed water molecules, bicarbonate ions, or hydroxyl ions from the calcite surfaces [13]. Multilayer adsorption seems to also occur at specific sites on calcite surfaces. Adsorption of phosphate can take place on a limited number of sites, and as the site coverage increases, lateral interaction occurs between the adsorbed phosphate and free ions. These clusters can serve as heteronuclei from which spontaneous crystal growth can occur [10]. At high phosphate concentrations, the reaction between phosphate and calcite surfaces starts with small amounts of phosphate adsorption, followed by precipitation as dicalcium, brushite, octacalcium phosphate, and HAP [4,11]. As the concentration of phosphate increases, debris appears on the surface in the form of small lumps about 1 μm in diameter and coral-like porous hemispherical growths on the faces and edges of the crystals [11]. pH plays an important role in the removal of phosphate. In solutions with low phosphate concentrations, high pH favors the removal process of phosphate species. At pH levels between 7.0 and 8.2, adsorption seems to result from electrostatic and chemical interactions [3]. A study examining solutions with high phosphate concentrations and pH in ranging from 4 to 12 showed that the highest phosphate removal efficiency was obtained in the pH range of 6 to 7, and the efficiency decreased with increasing pH [4].

Many cations and anions (such as Mg2+, Ca2+, CO3 2−, SO4 2−, etc.) in industrial wastewater may also affect phosphate removal by calcite. The presence of Mg2+ and Ca2+ can increase the adsorption of phosphate by calcite because these cations can form CO3−–Mg−PO4−
and CO$_3^-$ – Ca – PO$_4$ bonds at the carbonate sites on the calcite surface [12]. Adding SO$_4^{2-}$ to the solution may lower the activity of these cations due to the formation of sulfate ion pairs (MgSO$_4$ and CaSO$_4$), and thus reduce phosphorus adsorption. The adsorption of phosphate on calcite is almost independent of salinity, but is strongly influenced by bicarbonate concentration [12]. Fluoride can decrease phosphate removal regardless of pH because fluoride competes for calcium to form CaF$_2$ [4,14,15].

There is currently no data available on the effect of sulfate on phosphate removal and the kinetics of phosphate removal by calcite at high phosphate concentrations. The objective of this study was to investigate the effects of sulfate on high-concentration phosphate removal by calcite at different pHs.

### 2. Experiment methods

#### 2.1. Materials and chemicals

A natural calcite sample was mined from Zhenjiang County (China), and the content of calcium carbonate was 98.4% wt. The calcite sample was manually ground, and particles between 80 and 100 mesh were selected. A solution containing 1000 mg P/L phosphate (P stock solution) was prepared by dissolving pure KH$_2$PO$_4$ in distilled water. The pH of the initial phosphate solution was then adjusted to desired values using KOH or HCl solutions.

2.2. Influence of pH on removal of phosphate

The effect of pH on phosphate removal was evaluated at different initial pH values (3.0–13.0) at room temperature (25 °C) for 48 h. Exactly 1.00 g calcite and 50 mL of solution with a P concentration of 1000 mg/L (pH pre-adjusted to the desired value) were mixed in a 150 mL flask. The mixture was stirred at 150 rpm at 25 °C in a thermostatic shaker. After 48 h, the suspension was filtered through a 0.45 μm cellulose acetate membrane and the filtrate was analyzed for residual phosphate.

2.3. Influence of sulfate on removal of phosphate

Synthetic wastewater solutions were prepared by mixing K$_2$SO$_4$ and KH$_2$PO$_4$ at various molar ratios of SO$_4^{2-}$/PO$_4^{3-}$ (1.5, 3.0, 6.0, 10.5, 15.0) while the concentration of phosphate was kept at 1000 mg P/L and the pH of the mixture was adjusted to 4.5 and 13.0. Exactly 1.00 g of calcite and 50 mL of each solution were mixed in a flask, and the procedures for equilibrium and measurement were as previously described.

2.4. Phosphate removal process

To understand the process of phosphate removal, kinetic experiments were conducted at different pH levels with a P concentration of 1000 mg/L at a temperature of 25 °C. Exactly 3.00 g of calcite was added to a 1000-mL flat-bottomed flask that contained 1000 mL of phosphate solution at pH 4.5 or 13.0 with or without K$_2$SO$_4$ (SO$_4^{2-}$/PO$_4^{3-}$ = 15.0). The flasks were magnetically stirred. About 1.5 mL aliquots of solution were collected at desired time intervals. The solution samples were filtered and analyzed as described above.

2.5. Product analysis

To determine morphological changes on the calcite surface, XRD analysis was conducted on the precipitate using a D/Max2200 X-ray diffractometer (Rigaku Corp., Tokyo, Japan) with CuKa radiation (40 kV, 40 mA) and a Ni filter, scanned from 3.0° to 50.0° with a scan speed of 4.0°/min.

### 3. Results and discussion

#### 3.1. Effect of pH

Fig. 1 shows the relation between the pH and phosphate removal at 48 h. When initial pH was increased from 3.0 to 5.0 (the final pH from 6.6 to 7.7), the phosphate removal increased with increasing pH. Phosphate removal decreased with the increase of initial pH from 5.0 to 10.0 (final pH from 7.7 to 9.2). Less efficient phosphate removal was observed at an initial pH range from 8.0 to 11.0, and the removal efficiency was then increased with the increase of pH from 10.0 to 13.0 (final pH from 9.2 to 13.0).

The effect of pH on phosphate removal can be attributed to changes in the surface sites or speciation of phosphorus in the solution as well as the dissolution of calcite [4,12]. The effect of pH on phosphate removal is also related to the degree of supersaturation and the type of precipitates formed [4]. As we know, when phosphate or calcite exists in water, the following chemical species will be formed by the following reactions at 25 °C [3,17–20].

\[
\begin{align*}
\text{PO}_4^{3-} + 2\text{H}_2\text{O} &\rightarrow \text{HPO}_4^{2-} + \text{OH}^- & \text{pK} = 1.68 \\
\text{HPO}_4^{2-} + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{PO}_4^- + \text{OH}^- & \text{pK} = 6.79 \\
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{PO}_4 + \text{OH}^- & \text{pK} = 11.67 \\
\text{H}_2\text{O} &\rightarrow \text{H}^+ + \text{OH}^- & \text{pK} = 14 \\
\text{CaCO}_3(s) &\rightarrow \text{CaCO}_3(aq) & K_1 = 10^{-3.09} \\
\text{CaCO}_3(aq) &\rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} & K_2 = 10^{-3.25} \\
\text{CO}_3^{2-} + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{CO}_3^- + \text{OH}^- & K_3 = 10^{-3.67} \\
\text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} + \text{H}^+ & K_4 = 10^{-1.65} \\
\text{H}_2\text{CO}_3^- &\rightarrow \text{CO}_3^{2-}(g) + \text{H}_2\text{O} & K_5 = 10^{1.47} \\
\text{Ca}^{2+} + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{CO}_3^+ & K_6 = 10^{0.82} \\
\text{CaHCO}_3^- &\rightarrow \text{H}^+ + \text{CaCO}_3(aq) & K_7 = 10^{-7.80}
\end{align*}
\]

![Fig. 1. Effect of initial pH on phosphates removal.](image-url)
Ca\textsuperscript{2+} + OH\textsuperscript{-} \rightarrow \text{CaOH}\textsuperscript{+} \quad K_8 = 10^{1.40} \quad (12)

CaOH\textsuperscript{+} + OH\textsuperscript{-} \rightarrow \text{Ca(OH)}\textsubscript{2}(aq) \quad K_9 = 10^{1.87} \quad (13)

Ca(OH)\textsubscript{2}(aq) \rightarrow \text{Ca(OH)}\textsubscript{2}(s) \quad K_{10} = 10^{2.45} \quad (14)

The protonation reactions (1)–(4) are also illustrated in the speciation diagram shown in Fig. 2.

Using the equilibrium constants given in Eqs. (5) to (14), one can evaluate the isoelectric point (IEP) from the available data by calculating the concentrations of various species in equilibrium with calcite at different pH values [17]. The results indicate that IEP is attained at pH 8.4 [17]. When a solution is in equilibrium with a solid phase, IEP will often be found at the pH of minimum solubility.

Under equilibrium conditions, the region of minimum total dissolved solid phase, IEP will often be found at the pH of minimum solubility. At pH 8.4 [17], when a solution is in equilibrium with a solid phase, IEP will often be found at the pH of minimum solubility.

The results indicate that IEP is attained at pH 8.4 [17]. When a solution is in equilibrium with a solid phase, IEP will often be found at the pH of minimum solubility.

At pH 8.4 (Fig. 1), this confirms that the dissolution of calcite is important for phosphate removal.

When the initial pH was from 3.0 to 5.0, the final pH was from 6.6 to 7.7 (Fig. 1). This final pH range, dissolved calcite was mainly in the forms of Ca\textsuperscript{2+}, CO\textsubscript{3}\textsuperscript{2-}, and HCO\textsubscript{3}-, while phosphorus species should be mainly in the forms of H\textsubscript{2}PO\textsubscript{4} and HPO\textsubscript{4}\textsuperscript{2-} (Fig. 2). The removal process can be described through the following reactions:

\[ \text{Ca}^{2+} + \text{H}_2\text{PO}_4^{-} = \text{CaH}_2\text{PO}_4^{+} \quad \text{pK} = -1.08 \quad (15) \]

\[ \text{Ca}^{2+} + \text{HPO}_4^{2-} = \text{CaHPO}_4 \quad \text{pK} = -7.0 \quad (16) \]

As the initial pH levels of the phosphate solution varied from 5.0 to 10.0, the final pH levels ranged between 7.7 and 9.2. At these pH levels, HPO\textsubscript{4}\textsuperscript{2-}, Ca\textsuperscript{2+}, and CO\textsubscript{3}\textsuperscript{2-} were the predominant forms. The removal process can be described through the following reactions [23–25].

\[ \text{Ca}^{2+} + \text{HPO}_4^{2-} = \text{CaHPO}_4 \quad \text{pK} = -7.0 \quad (16) \]

\[ 10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^{-} = \text{Ca}_{10}[(\text{PO}_4)_{6}\text{OH}]_2 \quad \text{pK} = -126 \quad (17) \]

\[ 10\text{CaCO}_3 + 2\text{H}^{+} + 6\text{HPO}_4^{2-} + 2\text{H}_2\text{O} = \text{Ca}_{10}[(\text{PO}_4)_{6}\text{OH}]_2 + 10\text{HC}O_3^{-} \quad \text{pK} = -32 \quad (18) \]

However, as the initial pH of the phosphate solution varied between 10.0 and 13.0, the final pH levels were from 9.2 to 13.0. At these pH values, HPO\textsubscript{4}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}, CaCO\textsubscript{3}, Ca\textsuperscript{2+}, and CaOH\textsuperscript{+} were the main forms in the solution. The removal process can be described through the following reaction [20]:

\[ 10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^{-} = \text{Ca}_{10}[(\text{PO}_4)_{6}\text{OH}]_2 \quad \text{pK} = -126. \quad (17) \]

### 3.2. Impact of sulfate on removal of phosphate

In this work, the removal of phosphate with or without added sulfate at various concentrations was studied at 48 h and at pH 4.5 or 13.0 (Fig. 3). Compared to the results without the addition of sulfate at pH 4.5, low SO\textsubscript{4}\textsuperscript{2-}/PO\textsubscript{4}\textsuperscript{3-} ratios of 1.5 and 3.0 enhanced the removal of phosphate. Because sulfate increased dissolution of calcite and promoted calcium release from calcite, more brushtite could form. The solubility of calcite in a solution coexisting with sulfate ions can be several times greater than that of pure water because of the salt effect and ion pairs when common ions do not exist in solution; furthermore, the solubility of calcite increases with increasing sulfate concentration [26]. At higher sulfate concentrations (where the ratio of SO\textsubscript{4}\textsuperscript{2-}/PO\textsubscript{4}\textsuperscript{3-} is 6.0, 10.5, or 15.0), sulfate inhibited phosphate removal.

This may be due to the formation of calcium sulfate and calcium phosphate phases that co-precipitate on the calcite surface in a solution of coexisting sulfate and phosphate. This would also inhibit the removal of phosphate.

At the initial pH of 13.0, the effect of sulfate on the phosphate removal appeared to be different from that at the initial pH of 4.5 (Fig. 3). Low sulfate concentration (SO\textsubscript{4}\textsuperscript{2-}/PO\textsubscript{4}\textsuperscript{3-} ratios of 1.5 and 3.0) seemed to have little influence on phosphate removal in 48 h. At higher concentrations (SO\textsubscript{4}\textsuperscript{2-}/PO\textsubscript{4}\textsuperscript{3-} ratios of 6.0, 10.5, and 15.0), however, the phosphate removal increased with increasing sulfate concentration. As we know, free calcium decreases in strong alkaline conditions. A high concentration of sulfate in the solution can promote the release of calcium from calcite to possibly form hydroxyapatite, which will increase phosphate removal.

### 3.3. Processes of phosphate removal

To understand the processes of phosphate removal by calcite under high concentrations of sulfate at acidic and basic solutions, the residual phosphate concentration was plotted as a function of reaction time with SO\textsubscript{4}\textsuperscript{2-}/PO\textsubscript{4}\textsuperscript{3-} ratios of 15.0 at pH 4.5 or 13.0, and at

![Fig. 2. Phosphate distribution curves.](image1)

![Fig. 3. Phosphate removal at different sulfate concentration at 48 h.](image2)
low calcite dose (3 g/L). Figs. 4–5 show dramatic S-curves. The ultimate solid reaction products were pH and sulfate dependent (see Fig. 6). Brushite appeared to be the dominant form of precipitation when sulfate was absent whereas HAp became the dominant form of precipitation when sulfate was present at pH 4.5. At pH 13.0, the precipitate was mainly HAp regardless of the presence of sulfate.

From Fig. 4, large differences between the kinetic rates of removal were suggested. Quantitatively, more phosphate ions were removed without sulfate than were with sulfate at pH 4.5 at equilibrium time. Without the addition of sulfate, it seemed that the phosphate removal process occurred in three steps: (1) the concentration of phosphate was almost unchanged before 6 h in the first stage because calcium required time to release from calcite; (2) the concentration of phosphate decreased sharply in the middle stage (between 6 h and 60 h), and calcium was released continuously from calcite while brushite formed simultaneously; and (3) the removal process reached equilibrium in the third stage. In the presence of sulfate, the phosphate removal process apparently followed four steps. In the first stage, the concentration of phosphate did not decrease substantially in the first 84 h. Some syngenite formed in the intermediate product (see Fig. 7), and the intensity of its XRD peak increased with increasing time. By contrast, the intensity of calcite’s XRD peak decreased. The dissolution of the calcite supplied the calcium required for the precipitation of syngenite firstly because the concentration of sulfate was much greater than that of phosphate. This could account for the concentration of phosphate remaining almost unchanged during this stage. In the second stage, the concentration of phosphate decreased sharply between 84 h and 108 h. Because syngenite is a relatively soluble calcium-rich phase [28], it was eventually converted into HAp with phosphate, providing a continuous supply of calcium. Furthermore, syngenite facilitated a reaction between calcium and phosphate ions to form HAp as below [29]:

$$10K_2SO_4 \cdot CaSO_4 \cdot 2H_2O + 6HPO_4^{2−} \rightarrow Ca_{10}(PO_4)_{6}(OH)_2 + 8H^+ + 10SO_4^{2−} + 10K_2SO_4 + 18H_2O.$$  (19)

In the third stage, the phosphate concentration decreased slowly between 108 h and 132 h. During this stage, more complex reactions occurred, such as the formation of syngenite and reactions (19). The HAp formation on the calcite surfaces prohibited further release of free calcium ions from the calcite because calcites were used as seeds to form HAp. This was followed by nucleation and growth on the surface of calcite crystals [22,24], which consequently deterred the removal of phosphate. In the fourth stage, the removal process reached equilibrium. According to the molecular structural formulas, the formation of HAp requires more calcium ions than does the formation of brushite, suggesting that calcium ions might be the limiting factor in this system, resulting in removing more phosphate without sulfate than would occur with sulfate.

The kinetic curves at initial pH 13.0 were generally smooth, and the difference in phosphate removal in the absence or presence of sulfate was small. The phosphate removal rate was faster with added sulfate than without it. HAp and calcite were found regardless of the presence of sulfate (Fig. 6). The removal process could be divided into three steps (Fig. 5). When sulfate was present, the concentration of phosphate was almost unchanged in the first 2 h, followed by a quick decrease and then a slow finalization culminating in equilibrium. Similar processes occurred when sulfate was absent except that equilibrium was reached hours later. The pH at equilibrium was almost unchanged. HAp was easy to form because PO$_4^{3−}$ was the dominant phosphate ion at this pH. Although sulfate was in oversupply, it is impossible to form calcium sulfate as a precursor because calcium sulfate is much more soluble than is HAp. The existence of sulfate can promote the solubility of the calcite, which would, in turn, promote greater release of calcium from calcite; thus, the removal of phosphate with sulfate was faster than that without sulfate. Some calcite crystals were not consumed by the formation of HAp because they served as seeds for HAp formation on their surfaces.
To analyze the time response in the absence and presence of sulfate ions, four kinetic models (first-order, second-order, parabolic diffusion, and Elovich) were used to test the experimental data [30]. These classic kinetic models, respectively, are expressed as:

\[
\ln C_t = \ln C_0 - k_1 t, \quad (20)
\]

\[
\frac{1}{C_t} = \frac{1}{C_0} + k_2 t, \quad (21)
\]

\[
\frac{C_t}{C_0} = a + k_3 t^{1/2}, \quad (22)
\]

\[
C_t = b + k_4 \ln t, \quad (23)
\]

where \(C_t\) (mg/L) and \(C_0\) (mg/L) is the concentration at time \(t\) (h) and the initial concentration, \(k_1\) (h\(^{-1}\)), \(k_2\) (L/(mg·h)), \(k_3\) (h\(^{-0.5}\)) and \(k_4\) (mg/L) is the first-order, second-order, parabolic diffusion, and Elovich equations rate constant, respectively; and \(a\) and \(b\) are the intercept of parabolic diffusion and Elovich equation.

As shown in Table 1, the four classic kinetic models (first-order, second-order, parabolic diffusion, and Elovich) failed to adequately describe phosphate removal by calcite. Deviation from these kinetic models arises when multiple chemical and transport processes influence the total reaction rate [30,31]. Despite this complexity, the phosphate removal mostly occurred during the middle stage. Therefore, we used the above-mentioned kinetic models to test the middle stage (Table 2). The middle stage could be described by these four kinetic models except at initial pH 4.5 with sulfate addition. At initial pH 4.5 with sulfate addition, the middle stage could be divided into two stages. Between 84 and 108 h, the four kinetic models fit the data, and between 108 and 240 h, the stage was fitted by second-order and Elovich equations (see Table 2).

### Table 2

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Reaction period (h)</th>
<th>First order</th>
<th>Second order</th>
<th>Parabolic diffusion</th>
<th>Elovich</th>
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</thead>
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<tr>
<td>pH = 4.5</td>
<td>8–60</td>
<td>0.949</td>
<td>0.989</td>
<td>0.954</td>
<td>0.991</td>
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<tr>
<td></td>
<td>84–240(^a)</td>
<td>0.744</td>
<td>0.825</td>
<td>0.711</td>
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<td>108–240(^a)</td>
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<td>0.999</td>
<td>0.980</td>
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<tr>
<td>pH = 13</td>
<td>6–120</td>
<td>0.982</td>
<td>0.994</td>
<td>0.991</td>
<td>0.957</td>
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<td></td>
<td>4–84(^a)</td>
<td>0.986</td>
<td>0.995</td>
<td>0.997</td>
<td>0.958</td>
</tr>
</tbody>
</table>

\(^a\) Sulfate ions addition.

The curves in Figs. 4–5 were S-type. Therefore, a logistic model [32] (Eq. (24)) was also tried to describe the whole curves; the calculated parameters are presented in Table 3.

\[
y = A_2 + (A_1 - A_2)/(1 + (t/t_{50})^p) \quad (24)
\]

The logistic model is usually used to describe growth or diffusion with a limiting factor. The data fit the logistic model well with \(r^2\) values greater than 0.98. \(A_1\) (mg/L) is the initial concentration and \(A_2\) (mg/L) is the final concentration. The range between \(A_1\) and \(A_2\) is the dynamic signal range. \(t_{50}\) (h) is the time when the phosphate removal was half of the value of \(A_1 + A_2\), and \(p\) is the slope at the inflection point of the sigmoid curve. The parameters of the logistic model were calculated and are listed in Table 3.

Figs. 4–5 show that the predicted \(A_{cal}\) values from the logistic equation agreed very well with the experimental \(A_{exp}\) values. The logistic model seemed to have remarkable determination coefficients. The calculated parameters from the logistic model are given in Table 3. The logistic model appeared to be the most suitable model for describing the process of phosphate removal by calcite.

From the best fit of the logistic function, \(t_{50}\) and the curve slope were estimated. At pH 4.5 with added sulfate, the point of inflection \((t_{50})\) determined from the logistic model was longer than that without sulfate, indicating that the removal of phosphate without added sulfate occurred faster than that with sulfate. This most likely happened because the formation of syngenite inhibited the phosphate removal. The \(p\) value was greater with sulfate addition than that without sulfate, suggesting that the phosphate removal rate was quicker with sulfate addition at the inflection point of the curve because syngenite was a relatively soluble calcium-rich phase and a fast-releasing calcium source. The residual concentration of phosphate \((A_2)\) without sulfate addition was less than that with sulfate addition. This was related to the final reaction products—brushite (CaHPO\(_4\)·2H\(_2\)O) in the absence of sulfate and HA\(_p\) (Ca\(_{10}\)(PO\(_4\)\(_3\))\(_{6}\)(OH)\(_2\)) in the presence of sulfate, which needs more calcium ions in the presence of sulfate. In this system, calcium was obviously the limiting factor. At the initial pH of 13.0, \(t_{50}\) value was greater without sulfate addition than that with sulfate addition. This implied that the removal of phosphate with added sulfate was faster than that without sulfate because of the fast release of calcium from calcite in the presence of sulfate. The residual concentration of phosphate \((A_2)\)

### Table 1

<p>| Coefficients of determination ((r^2)) for the fit of the time dependence of phosphate removal by calcite with or without sulfate at pH 4.5 and pH 13.0 to several kinetic models. |
|-------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|</p>
<table>
<thead>
<tr>
<th>Kinetic equation</th>
<th>pH = 4.5 Without sulfate</th>
<th>pH = 4.5 With sulfate</th>
<th>pH = 13.0 Without sulfate</th>
<th>pH = 13.0 With sulfate</th>
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</thead>
<tbody>
<tr>
<td>First order</td>
<td>0.565</td>
<td>0.728</td>
<td>0.911</td>
<td>0.846</td>
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<tr>
<td>Second order</td>
<td>0.604</td>
<td>0.818</td>
<td>0.939</td>
<td>0.876</td>
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<tr>
<td>Parabolic diffusion</td>
<td>0.756</td>
<td>0.815</td>
<td>0.962</td>
<td>0.933</td>
</tr>
<tr>
<td>Elovich</td>
<td>0.863</td>
<td>0.722</td>
<td>0.775</td>
<td>0.833</td>
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</table>

### Table 3

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Equilibrium pH</th>
<th>(C_1) (mg/L)</th>
<th>(C_2) (mg/g)</th>
<th>(t_{50}) (h)</th>
<th>(p)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 4.5</td>
<td>7.8</td>
<td>994</td>
<td>301</td>
<td>17.9</td>
<td>2.44</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>7.8(^a)</td>
<td>991</td>
<td>384</td>
<td>108.4</td>
<td>4.00</td>
<td>0.981</td>
</tr>
<tr>
<td>s</td>
<td>13</td>
<td>973</td>
<td>419</td>
<td>45.5</td>
<td>1.90</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>13(^a)</td>
<td>982</td>
<td>411</td>
<td>34.3</td>
<td>1.55</td>
<td>0.994</td>
</tr>
</tbody>
</table>

\(^a\) Sulfate ions addition.
without sulfate addition is close to that with sulfate addition because the main reaction product takes the same form \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \).

4. Conclusion

High-concentration phosphate removal by calcite was favorable in both acidic and strong basic solutions in this study. The presence of sulfate significantly influenced phosphate removal by calcite. Low concentrations of sulfate in acidic conditions could promote phosphate removal, but high sulfate concentrations could inhibit phosphate removal because calcium sulfate formed first (as a precursor). Under strong basic conditions, phosphate removal increased with increasing sulfate. Phosphate removal occurred primarily through a process beginning with the dissolution of calcite followed by the precipitation of variable brushite-type under acidic conditions and Hydroxyapatite (HAp) under alkaline conditions. The process for high-concentration phosphate removal by calcite was much more complex. Classic kinetic models (i.e., first-order, second-order, parabolic diffusion, and Elovich) were unable to describe the observed results. The whole kinetic process fit a logistic model, regardless of the presence of sulfate. Thus, process engineers should remember that pH and concentration of sulfate do matter and that a logistic model can be used to predict the outcome of the phosphate/calcite treatment process.

Acknowledgments

We express sincere gratitude to the National Natural Science Foundation of China (20907058) for the financial support in this research.

References