



Removal properties of phosphate with Ettringite

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ABSTRACT

This work has performed the feasibility of utilizing synthetic ettringite as an adsorbent for phosphate removal in lab-scale experiments. Studies were focused on the influence of solution pH for the removal properties of phosphate. Ettringite was stable in the alkaline condition, and it was quickly decomposed in acid condition. Calcium and aluminum compound was formed at each pH condition. Phosphate removal performance was increased with the increase of solution pH. It was shown that the phosphate removal mechanism was influenced not only ion-exchange but also phosphate compound formation. The inside of large size ettringite residue was kept ettringite structure, and the phosphate was removed by ettringite surface only.

Keywords: Adsorption; Alkaline condition; Cement precursor; Ettringite; pH; Phosphate

1. Introduction

Whereas, the phosphate is considered as one of the important resources for various industrial and agricultural purposes, many countries over the world are trying to control the careless use of phosphate for the protection of safe water environment.

Phosphate anion concentration exceeding approximately 2 μM in water bodies is able to stimulate algae growth which is related to eutrophication. Eutrophication, especially in lake and bay, is caused by nutrient salts such as potassium, nitrogen and phosphorus [1]. Phosphorus removal is more efficient than nitrogen removal to prevent eutrophication. However, phosphorus removal efficiency is not satisfactory enough to prevent eutrophication. Although, the conventional process for P removal from wastewater treatment plant is release followed by luxurious uptake called as biological nutrients removal, Coagulation, and precipitation are extensively accepted

processes of phosphate removal in considering several merits like the simplification of maintenance, stable running, and treatment efficiency. These physicochemical treatment methods are able to treat phosphate. In most countries, phosphorus is not self-support element. Major producing countries of phosphorus are China, Morocco, and America. Phosphorus is positioned as a strategic material in China and America, so phosphorus is embargo material in these countries. Phosphorus recycling technology is required in recent years. A major recycling source of phosphorus is domestic and industrial wastewater and the ash of activated sludge [2]. Phosphorus in wastewater is treated by flocculation which needs a lot of reagents and disposes excess sludge [3]. Crystallization method can recover as valuable resources [4], but it is required special equipment and high technique of operation and maintenance. The adsorbent method is easy maintenance and hardly generates excess sludge. In addition, the method is able to recover phosphorus from saturated adsorbent when it is regenerated to usable adsorbent. Many adsorbents have been developed for phosphorus removal: aluminum oxide [5], iron oxide [6], dolomite [7], calcite [8],

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manganese dioxide [9], titanium dioxide [10], layered double hydroxide [11], zirconium oxide [12], ion-exchange resin [13]. Considering the aspects of material recovery, the ettringite is one of the most suitable minerals because it is simply synthesized from waste streams.

Ettringite is a hydrous calcium alumina-sulphate mineral and intermediate during cement production. Ettringite is expressed as follows: $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_6 \cdot 24\text{H}_2\text{O}$. Since, ettringite appears as a morphologically hexagonal prism or needle, the probability to act as a host for the immobilization of both cationic and anionic pollutants is expected in the employment of sorption process.

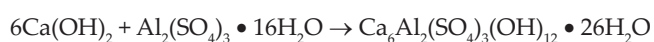
It is exchanged SO_4^{2-} in ettringite for anions in solution. So, it has been reported that ettringite has a capacity of adsorption for anions: arsenate [14], boron [15], fluorine [16]. Ion selectivity of ettringite has been examined, and the stable pH of ettringite was reported to be around 12 [17].

In this work, the synthetic ettringite was prepared for the removal of phosphorus as an adsorbent and examined the removal properties. We focused on the influence of solution pH for phosphorus removal performance and mechanism.

2. Materials and methods

2.1. Ettringite

Ettringite was obtained by precipitation method. 22.9 mmol of $\text{Ca}(\text{OH})_2$ was added to a liter of deionized water and 3.82 mmol of dissolved $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, where the mixture of Ca/Al was 3 mol ratio. The mixed solution was shaken 5 min and ettringite was precipitated. Precipitation was collected by centrifugal separation (2500G, 3 min) and dried at 40°C for 24 h. Dried ettringite was crushed by mortar, and it was classified about 80 μm . The synthesized reaction of ettringite is expressed as follows



Ettringite was constructed by column which is made of $(\text{Ca}_6(\text{Al}(\text{OH})_6)_2 \cdot 24\text{H}_2\text{O})^{6+}$ and inter-column which are SO_4^{2-} and $2\text{H}_2\text{O}$. The SO_4^{2-} was held by electrostatic interaction into the column inside.

2.2. Analytical methods

Water quality is analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 3300DV, Perkin-Elmer, USA) and ion chromatography (IC850,

Metrohm, Swiss). Ca and Al were analyzed by ICP-AES. PO_4^{3-} and SO_4^{2-} were analyzed by ion chromatography. Ion chromatography was equipped with non-suppressor type anion analytical column (TSK-gel IC-Anion PW_{XL} , Tosoh, Japan). The analytical samples were filtered by 0.45 μm membrane filter.

The structure of ettringite was analyzed by X-ray diffractometer (XRD) and scanning electron microscope (SEM, JSM-6330F, JEOL, Japan) equipped with an energy dispersive X-ray analyzer (EDX). XRD (XRD-6100, Shimadzu, Japan) was equipped with Cu $\text{K}\alpha 1$ radiation and investigated material structure. The diffracted scan range was 5–60 degree with interval of 0.05 degree. The morphology of the ettringite was analyzed by SEM, and the element content of ettringite surface was examined by EDX.

2.3. Adsorption experiment

Adsorption properties were performed by batch type experiments. The phosphate solution was prepared with Na_2HPO_4 . The initial concentrations of phosphate were adjusted to 5 and 10 mmol L^{-1} . Initial pH of the suspensions was checked and adjusted to the desired pH by the addition of standard solution of 4N HCl and 1N NaOH. Ettringite was added to the phosphate solution, and the removal reaction was performed for 24 h at 25°C under rotary shaker or stirrer mixing condition with a magnetic bar.

3. Results and discussion

3.1. Stabilization of ettringite

The influence of concentration of each element from ettringite decomposition solution pH is shown in Fig. 1. SO_4^{2-} and Ca^{2+} ion were drastically decomposed within the several min under the acidic condition, and Al^{3+} ion also followed the same behavior after 15 min later. According as pH increased, the decomposition of all elements became gradually moderate. Al^{3+} ion was hardly decomposed under neutral and alkaline pH condition. It is reported that ettringite is not stable phase and can be converted to the other crystal phase in alkaline condition [17] and quickly decomposed in the acidic condition.

The XRD pattern of the residues in the pH conditions is shown in Fig. 2. The initial ettringite concentration was 5 g L^{-1} . All scale and tick labels of Fig. 2 are shown the same there. The solution pH was adjusted for 3, 7, 9, and 12.

The enough volume was not collected to analyze for XRD analysis at pH 3, where the concentration of SO_4^{2-} and Ca^{2+}

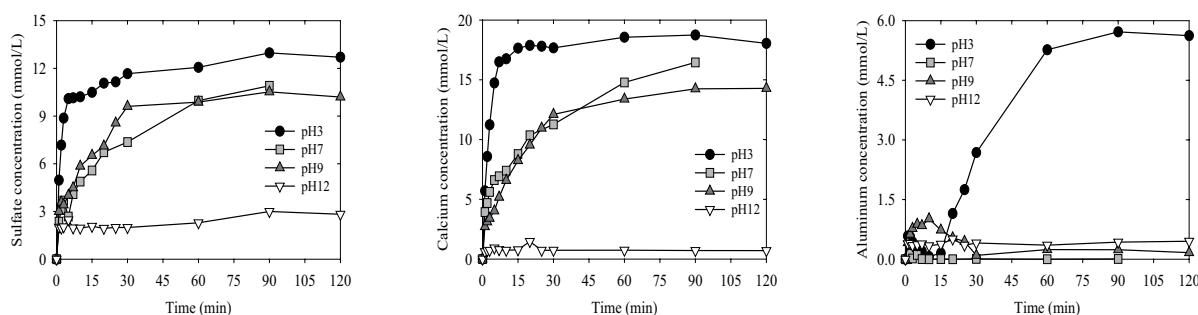


Fig. 1. Element concentration curves from ettringite decomposition in different solution pH.

were increased with time, and it was delayed 15 min for the increase of Al^{3+} concentration. The boundary pH between Al and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is changed by these concentration. It is depended on these concentration in a residues to convert between dissolved aluminum and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. In the low aluminum ion concentration, dissolved aluminum is converted to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ at pH 3. $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was attached to ettringite surface, because the pH of ettringite surface is higher than bulk area. From the behavior of calcium ion and sulfate concentration, most ettringite was decomposed about 15 min at pH3. After 15 min, pH was increased on the surface of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, it was converted to dissolved aluminum. At pH 7 and 9, ettringite was not detected by XRD analysis and SEM image. It was analyzed same chemical compound from the precipitations, and the concentration of elements was shown the same behavior. CaCO_3 was synthesized by calcium ion from the decomposition of ettringite and carbon acid from the atmosphere. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the precursor materials of cement as ettringite, it was observed that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was synthesized with the condition lacked of dissolved aluminum. At pH 12, ettringite was analyzed by XRD and pH 12 is the stable range of ettringite [17]. Sulfate is the essential component for the stabilization of ettringite, and was released from the decomposition of ettringite.

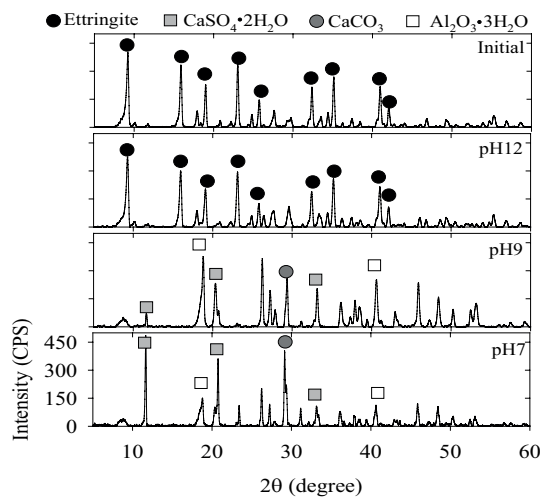


Fig. 2. XRD patterns of the residues in different pH conditions.

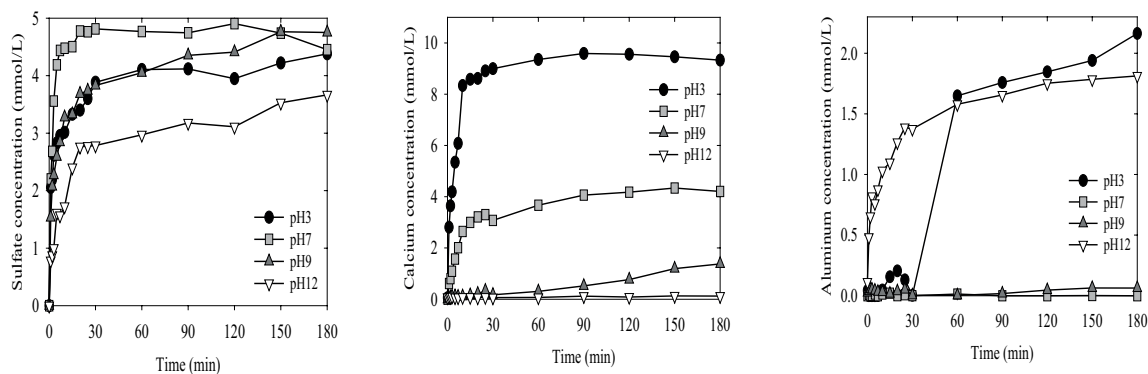


Fig. 3. The variation of elements concentration with adsorption time at various pH condition.

3.2. Effect of solution pH

In order to evaluate the influence of each element concentration on the solution pH of ettringite, the adsorption tests were performed at room temperature using several initial solution pH values changing from 3 to 12 as shown in Fig. 3.

SO_4^{2-} from ettringite was sharply released regardless of pH condition. While Ca^{2+} was observed under the neutral and acidic condition, Al^{3+} was monitored under alkaline condition. Although, SO_4^{2-} , Ca^{2+} and Al^{3+} were released from ettringite, all elements were less dependent on the specific pH condition.

The phosphate concentration was decreased with sorption time and stabilized within 120 min. Ettringite was not detected by XRD analysis from all samples. The time for the equilibrium of phosphate concentration was gradually increased with the increase of solution pH. However, the phosphate removal ratio was not influenced by the solution pH.

The XRD pattern of the residual materials from each pH conditions is shown in Fig. 5. Initial phosphate concentration was 5 mmol L^{-1} and initial ettringite concentration was 2 g L^{-1} . All scale and tick labels of Fig. 5 without XRD pattern of “initial” are shown the same there.

While, SO_4^{2-} and Al^{3+} concentrations after the phosphate removal experiment were increased at pH 12, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ was detected by XRD analysis. As XRD peak of ettringite was detected, the equilibrium situation on the ettringite

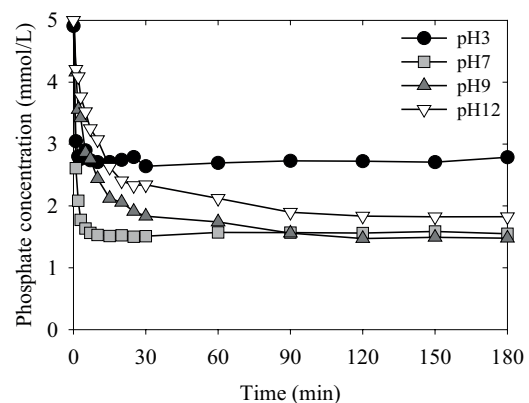


Fig. 4. The profile of phosphate adsorption capacity with adsorption time at various pH condition.

surface was not maintained by the formation of phosphate compound.

These different behaviors are influenced by the formation of phosphorus compounds. The SO_4^{2-} concentration at pH 7 and 9 is higher than that of pH 3, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was not detected from XRD analysis. Ca^{2+} and Al^{3+} ion concentrations at pH 7 and 9 were lower than at pH 3. It is suggested that Ca^{2+} and Al^{3+} ions are formed with phosphate at pH 7 and 9. The residues of pH 7 and 9 were treated at 700°C and the heat-treated residuals were detected by the XRD peak pattern of $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ at pH 9. Calcium phosphate compounds were not detected by XRD analysis. The residue at pH 7 was dissolved by HNO_3 . The content is as follows: phosphorus is 38 mol%, sulfur is 1 mol%, calcium is 45 mol%, aluminum is 16 mol%. At pH 7 and 9, it was shown that the phosphate was removed by the formation of calcium and/or aluminum phosphate compounds. As the behavior of decrease with phosphate concentration consistent with increase in aluminum concentration, phosphate was removed by the combination of aluminum phosphate compounds at pH 3.

The removal mechanism of ettringite for hazardous component is reported to be an ion-exchange reaction [14–16]. The phosphate removal amount compared with the calculated value of ion-exchange reaction and the compound formation is shown in Fig. 6, where the initial phosphate concentration was 10 mmol L^{-1} . The values of ion-exchange were calculated by phosphate ion valences. The values of compound formation were calculated assuming that phosphate forms $\text{Ca}_3(\text{PO}_4)_3\text{OH}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ from all calcium and aluminum content of ettringite. Observed phosphate removal amounts were larger than calculated value for ion-exchange reaction at more than pH 7. Maximum phosphate removal can be obtained at pH 9, and the similar results were kept at neutral and alkaline pH condition. It is suggested that phosphate removal of ettringite approached the compound formation.

3.3. Recovery of phosphorus

The granular ettringite with particle size of about 1 mm was used for phosphate removal experiment. Initial phosphate concentration was 10 mmol L^{-1} and it was adjusted to pH 7. Ettringite was packed in nylon mesh bag and initial ettringite concentration was 2 g L^{-1} , where initial phosphate concentration was 10 mmol L^{-1} . All elements were shown the same behavior with different pH condition. The removal amount was decreased to 0.59 mmol g^{-1} because of getting larger particle size. The XRD and SEM image with element mapping analysis were shown in Figs. 7 and 8 at half a hour, respectively. The ettringite particle was cut for the observation of cross-sectional morphology both surface and inside.

Both ettringite peak pattern and crystal structure inside were observed by XRD analysis. From element mapping analysis shown in Fig. 8, phosphorus was observed in surface only and sulfur inside. The phosphorus layer was $15\text{--}30 \mu\text{m}$, and the layer was not increased with time. Ca^{2+} and Al^{3+} ions were detected all areas and phosphorus was formed calcium and/or aluminum compound at pH 7. It was shown that the phosphate removal was influenced by the formation of phosphate compound.

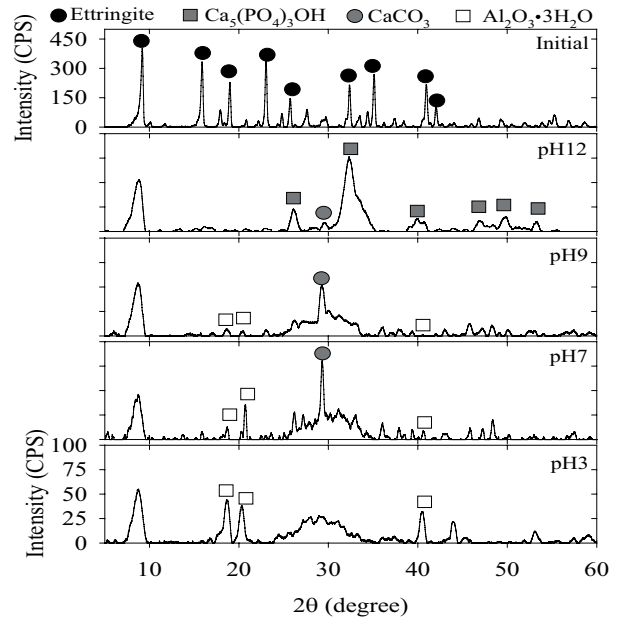


Fig. 5. XRD pattern of the residues in each pH conditions with ettringite and phosphate.

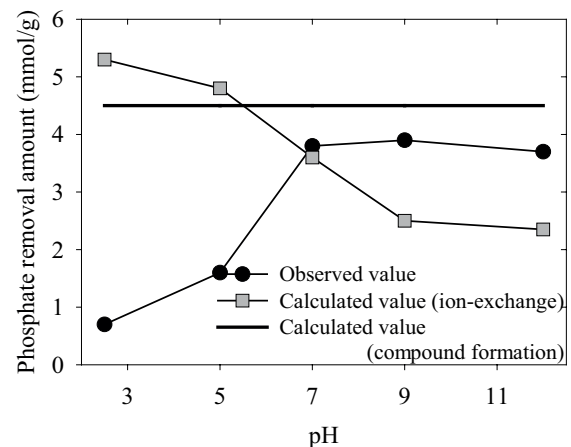


Fig. 6. Phosphate removal amount compared with calculated value of ion-exchange reaction and compound formation.

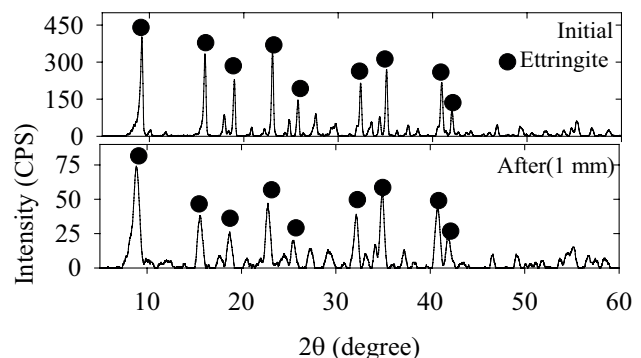


Fig. 7. XRD pattern of the ettringite 1 mm particle.

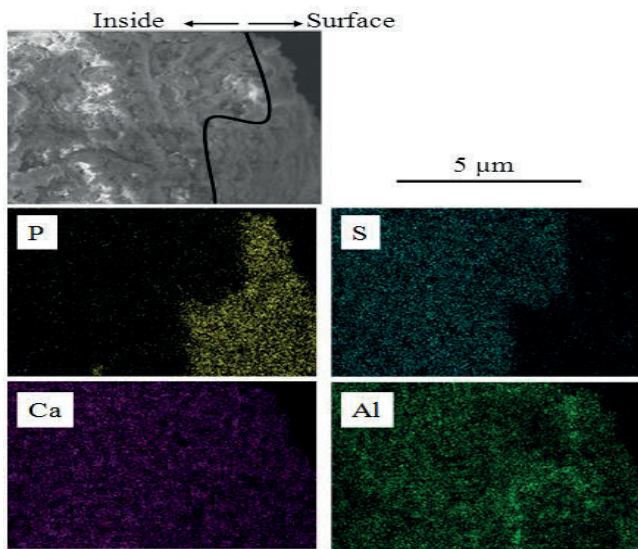


Fig. 8. SEM image with element mapping analysis of the ettringite 1 mm particle.

4. Conclusions

Ettringite was synthesized in order to remove phosphate as an adsorbent. The following conclusions can be drawn from the experimental results.

- (1) Synthetic ettringite was stable in alkaline condition and it was quickly decomposed in acid condition. Ca^{2+} and Al^{3+} ion compounds were formed at each pH condition.
- (2) Phosphate removal performance was increased with the increase of solution pH, which indicated that the phosphate removal mechanism was influenced not only ion-exchange but also phosphate compound formation.
- (3) The inside of large size ettringite residue was kept ettringite structure and phosphate was removed by ettringite surface only.

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