

HIGH EFFICIENT REMOVAL OF PHOSPHATE IN AQUEOUS SOLUTION BY ECO-FRIENDLY MATERIALS

Ho Hong Quyen^{1*}, Tran Vu Chi Mai¹

¹The University of Danang - University of Science and Technology

*Corresponding author: hhquyen@dut.udn.vn

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Abstract - The efficiency of phosphate removal in aqueous solution by CaO, Ca(OH)₂ and CaCO₃ has been studied in this work. Batch of experiments conducted with the initial phosphate concentrations from 5 to 1000 ppm have shown that CaCO₃ could be applied for phosphate removal at low concentration with the maximum phosphate removal capacity at 4.0 mg/g. In contrast, the highest phosphate removal capacity of CaO and Ca(OH)₂ was 287.36 mg/g and 235.21 mg/g at initial concentration of 500 ppm, and phosphate removal rate was 85% and 97% at initial concentration of 5 ppm. Crystalline hydroxylapatite was detected in the precipitate by XRD analysis. The molar ratio of P in the precipitate and Ca in the materials (CaO and Ca(OH)₂) was 0.52 and 0.56 at initial concentration of 500 ppm, compared to P/Ca molar ratio of 0.6 in hydroxylapatite. Moreover, hydroxylapatite is the main component of fertilizer that can be applied for agriculture.

Key words - Eutrophication; phosphate; precipitation; fertilizer; hydroxylapatite, high efficiency

1. Introduction

Phosphorus is an essential nutrient for the growth and development of plants. Nevertheless, the excessive phosphorus concentration from wastewater and biowaste flow including domestic wastewater, industrial wastewater (factories of food, beverage, paper and textile) agricultural wastewater, sludge and manure to water sources such as rivers, lakes and ponds leads to an algae bloom. This causes the reduction of water quality because of eutrophication. When eutrophication happens, the concentration of dissolved oxygen decreases rapidly. Furthermore, the bad odour and toxin appear and all of them will damage the ecosystem and derange the natural food chain [1]. Thus, phosphorus should be eliminated from domestic and industrial wastewater before being discharged into the aquatic environment.

Phosphorus arises in natural waters and in wastewater almost individually as phosphate. There are categorized as orthophosphate, condensed phosphate (pyro-, meta-, and other polyphosphates), and organically bound phosphates. These forms of phosphate occur from various sources. Orthophosphate and condensed phosphates are added to the water source during treatment, laundering and another cleaning. Organic phosphates are generated by biological process and contributed to sewage by food residues. They are also generated from orthophosphate in biological treatment processes [2]. There are numerous methods to remove phosphorus from aqueous solution such as membrane filtration, biological treatment and chemical precipitation [3]. Membrane filtration is an efficient method for the removal of phosphorus but high cost has limited its application in practice [4]. Biological technique is widely used in phosphorus removal in municipal

wastewater and food wastewater. However, the disadvantages of this method are the low removal speed and complex operation process [5]. Therefore, biological method is inappropriate in handling wastewater containing high phosphorus concentration. Chemical precipitation technique is used for treating industrial wastewater, which contains high concentration of phosphorus by employing aluminum salt or iron salts (Al₂(SO₄)₃, Fe₂(SO₄)₃, FeSO₄ and FeCl₃) to generate insoluble precipitates.

Nevertheless, the disadvantages of this method are the cost of chemicals and the management of chemical sludge after operation process since aluminum and iron in sludge are toxic for plants and human health [6]. Adsorption method using by-products from industries for phosphorus treatment has received attention recently since these materials are inexpensive. Blast furnace slag (BF slag), electric arc furnace slag (EAF slag) and basic oxygen furnace slag (BOF slag) discharged from steel factory have been extensively tested for phosphorus removal [7-8]. Steel slag can remove phosphorus because it contains heterogeneous oxides such as iron, calcium, aluminum and silicon oxides. Other wastes such as fly ash, peat, red mud, alunite, zeolite and oxide tailings used for phosphorus removal have been studied [9-11].

CaO (calcium oxide) and Ca(OH)₂ (calcium hydroxyl) are the products of the calcination of CaCO₃ (calcium carbonate) at high temperature. CaCO₃ is the main component of limestone which is a sedimentary rock found in geologic deposits or in sea animal shells and shell fragments, and these materials are considered to be available and inexpensive.

In this work, CaO, Ca(OH)₂ and CaCO₃ were used for phosphorus removal through batch of experiments. The target of this research is to transfer phosphorus in aqueous solution from soluble to insoluble to collect easily by filtration. Another target of this research is to improve the drawbacks of above methods, including the use of components from available and low-cost materials. Also, products after phosphate treatment could be recycled as a useful material. The product after reaction process was characterized by using an X-ray diffractometer (XRD).

2. Experiments

2.1. Materials and reagents

All chemicals reagents were analytically graded and used without further purification. CaO, Ca(OH)₂ and CaCO₃ was purchased from Kanto, Japan. Synthetic wastewater with different initial phosphate concentration

(5, 50, 500 and 1000 ppm) was prepared from potassium dihydrogen phosphate (KH_2PO_4) purchased from Kanto, Japan. Phosphorus standard solution (P 1000 ppm), $\text{C}_6\text{H}_8\text{O}_6$ (L(+)-Ascorbic acid), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Hexaammonium Heptamolybdate Tetrahydrate), sulfuric acid (H_2SO_4) were obtained from Kanto, Japan. $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2\cdot 3\text{H}_2\text{O}$ (Bis[(+)-tartrato] diantimonate (III) Dipotassium Trihydrate) was purchased from Fujifim Wako, Japan. Whatman 50 filter paper (2.7 μm particle retention) was purchased from International Ltd. Maidstone, England. All aqueous solutions were prepared using Mili-Q water from Direct-Q UV3, Merck Millipore.

2.2. Batch of experiments

0.1 g of CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3 each was added individually to 100 mL of phosphate solution at different initial phosphate concentrations (5, 50, 500 and 1000 ppm). The reaction was shaken vigorously at 25°C for 18 h in the water bath. After reaching the equilibrium state, the mixture was filtered to separate the supernatant and the solid for further examination. The pH of solution before and after the reaction was measured by using a pH meter (F-52, Horiba, Japan). The preparation of phosphorus standard solution with the range of concentration from 0.02 to 1.0 ppm is shown in Figure 1.



Figure 1. Samples of phosphorus standard solution (Phosphorus concentration 0.02; 0.2; 0.5 and 1.0 ppm)

The phosphate concentration of the samples before and after the experiment was examined by molybdenum blue method with ascorbic acid using UV-VIS method (UV/VIS/NIR Spectrophotometer V-570, Jasco, Japan) at a maximum wavelength of 880 nm. The same procedure was also employed with blank samples for each series of batch of experiments. The generation of molybdenum blue for phosphate examination is illustrated in Figure 2.

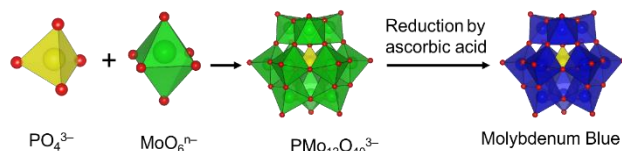


Figure 2. The formation of molybdenum blue for phosphate determination using UV/VIS/NIR Spectrophotometer

The efficiency of phosphate removal (H) and phosphate removal capacity (q_e) were determined by equation (1) and (2).

$$H = \frac{C_0 - C_e}{C_0} \cdot 100(\%) \quad (1)$$

$$q_e = \frac{C_0 - C_e}{M} \cdot V \text{ (mg/g)} \quad (2)$$

Where C_0 and C_e are the initial and equilibrium

concentrations of phosphate (ppm), respectively, M is the mass of materials CaO , $\text{Ca}(\text{OH})_2$ or CaCO_3 (g) and V is the volume of sample (L).

The molar ratio of P in the product after phosphate treatment and Ca in the material was calculated in Eq. 3:

$$\frac{\text{Moles of P}}{\text{Moles of Ca}} = \frac{m_{\text{P in product}} \left(\frac{\text{g}}{\text{mol}}\right)}{M_{\text{P}} \left(\frac{\text{g}}{\text{mol}}\right)} : \left(\frac{m_{\text{Ca in material}} \left(\frac{\text{g}}{\text{mol}}\right)}{M_{\text{material}} \left(\frac{\text{g}}{\text{mol}}\right)} \right) \text{ (mol/mol)} \quad (3)$$

Where $m_{\text{P in product}}$ and $m_{\text{Ca in material}}$ are the mass of P in product after phosphate removal and mass of Ca in material (g), and M_{P} and M_{material} are the molar mass of P and material (CaO , $\text{Ca}(\text{OH})_2$ or CaCO_3) (g/mol).

The product after filtration was dried at room temperature, then was placed on the silicon sample holder for XRD analysis. XRD measurement using SmartLab X-ray Diffractometer (Rigaku, Japan) was conducted with $\text{CuK}\alpha$ radiation of wavelength $\lambda = 1.5418 \text{ \AA}$. The X-ray generator worked at a power of 45 kV and the current of 200 mA. XRD patterns were collected in the 2θ range of 10 to 90° using a continuous scanning speed of 40° min^{-1} .

3. Results and discussion

3.1. Phosphate removal capacity by using CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3

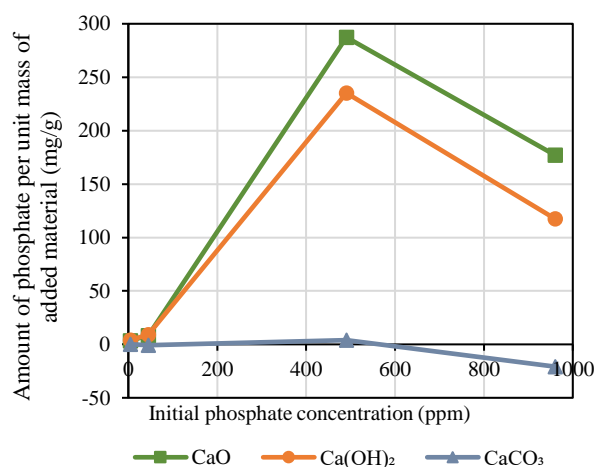


Figure 3. Capacity of phosphate removal by using CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3

Figure 3 shows phosphate removal capacity by using CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3 . The result revealed that the highest phosphate removal capacity of CaCO_3 was 4.0 mg/g at initial phosphate concentration of 500 ppm. Compared to CaCO_3 , the amount of phosphate in obtained product, which was collected from phosphate solution by filtration, was significantly high by using CaO , $\text{Ca}(\text{OH})_2$. In the range of initial phosphate concentration from 5 to 1000 ppm, mass of removal phosphate rapidly increased and reached a peak at 287.36 mg/g and 235.21 mg/g with initial phosphate concentration of 500 ppm by using CaO and $\text{Ca}(\text{OH})_2$, respectively. Nonetheless, phosphate removal decreased when initial concentration enhanced to 1000 ppm. The decline was attributed to the formation of the particles that their size was smaller than 2.7 μm of Whatman 50 filter

paper. Therefore, this kind of paper could not retain the small particles, leading to the phosphate still remaining in the filtered solution in the case of 1000 ppm.

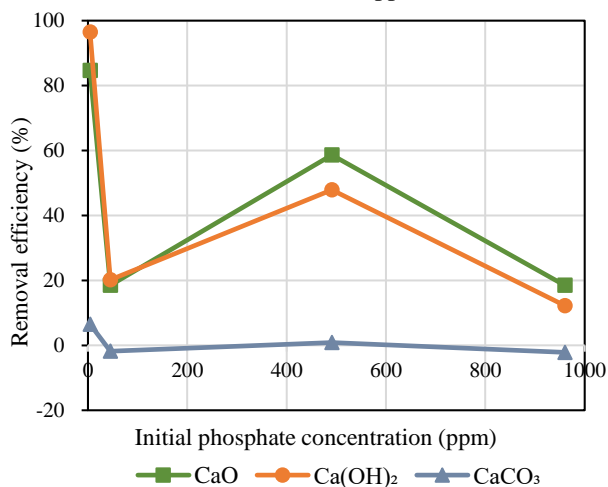


Figure 4. Phosphate removal efficiency by using CaO, Ca(OH)₂ and CaCO₃

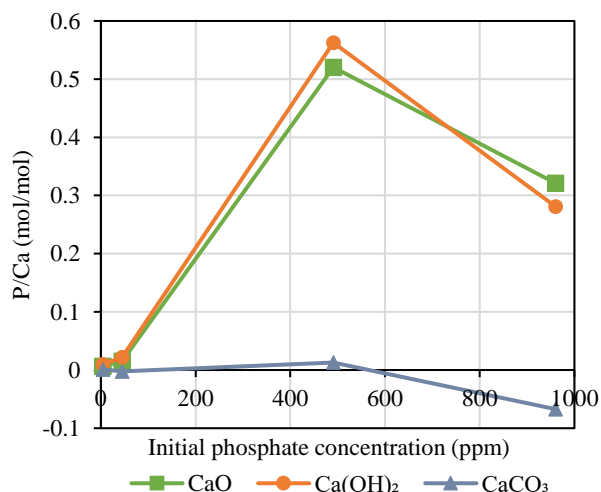


Figure 5. Effect of initial phosphate concentration on P/Ca (mol/mol) ratio

As shown in Figure 4, the phosphate removal rate was 85% and 97% at initial phosphate concentration of 5 ppm, and 59% and 48% at initial phosphate concentration of 500 ppm using CaO and Ca(OH)₂. In contrast, phosphate removal rate made up only 19% and 20% at initial phosphate concentration of 50 ppm by using CaO and Ca(OH)₂, respectively. From the observation of conducting the experiments of reaction and filtration, there was an appearance of particles with tiny size from the reaction of CaO and Ca(OH)₂ and phosphate solution in the samples of 50 ppm. This phenomenon indicates that the small size of particles produced from aqueous solution may pass through filter paper (2.7 μm particle retention) and could not be collected by filtration method. From the results of phosphate removal capacity and phosphate removal efficiency, it indicated that filter paper owning the pore size smaller than 2.7 μm was not effective for particles collection at initial phosphate concentration of 50 and 1000 ppm. It is essential to use filter paper with a smaller pore size or use flocculants/coagulants to combine the

small particles to become larger so that they can be removed from phosphate solution.

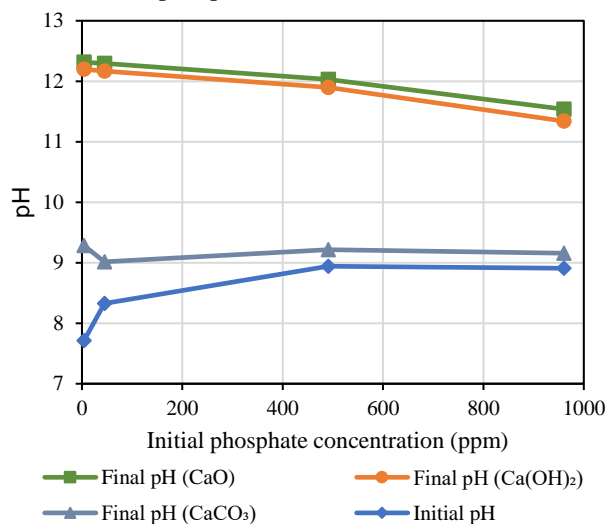


Figure 6. pH change of initial phosphate concentration and equilibrium phosphate concentration

The change trend of P/Ca molar ratio in product with increasing initial phosphate concentration was calculated, as presented in Figure 5. The value of P/Ca molar ratio rose dramatically and reached the highest level at 0.52 and 0.56 using CaO and Ca(OH)₂, respectively.

Different initial pH of phosphate solutions from 5 to 1000 ppm was recorded from 7.7 to 8.9. After adding various materials for phosphate treatment, the final pH of aqueous solution increased from 9.0 to 9.9 when using CaCO₃, and sharply rose from 11.5 to 12.3 when using CaO and Ca(OH)₂ (Figure 6). This finding has suggested that the solution after phosphate removal can be used to neutralize acidic soil for plants development.

3.2. Phosphate removal mechanism

After experiments of phosphate removal, the products were tested using XRD. As presented in Figure 7, XRD pattern of CaCO₃ sample exhibited the presence of calcite (CaCO₃). Thus, there was no reaction of and CaCO₃ and KH₂PO₄ solution. This finding from XRD analysis explained the low phosphate removal capacity and removal efficiency by using CaCO₃, which presented above results.

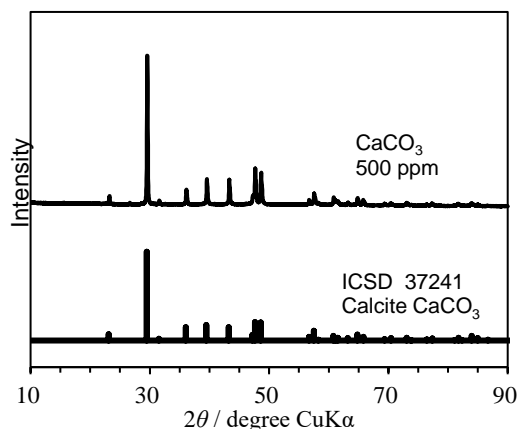


Figure 7. XRD of precipitate from the reaction of CaCO₃ and KH₂PO₄ solution

As shown in Figure 8, crystalline hydroxylapatite was found in the obtained particles from both CaO and Ca(OH)₂ samples at the initial concentration of 500 ppm. Assuming that all precipitates are hydroxylapatite and all precipitants react with phosphate, the molar ratio of P/Ca (mol/mol) in hydroxylapatite is 0.60 while this value from P in the product after phosphate treatment and Ca in the material including CaO and Ca(OH)₂ was 0.52 and 0.56 at initial phosphate concentration of 500 ppm (Figure 5). This suggested that the reaction between PO₄³⁻ ions and CaO or Ca(OH)₂ did not happen completely.

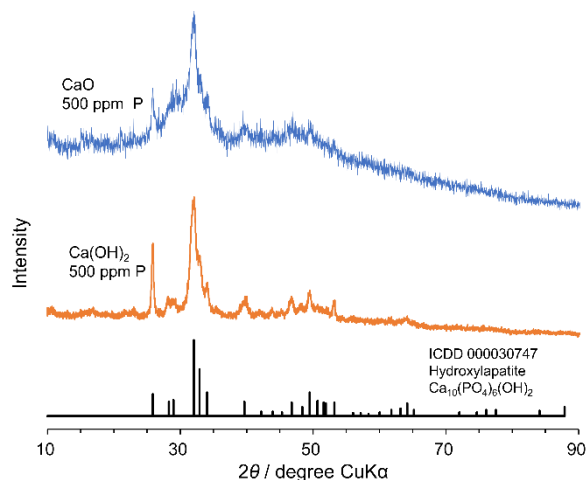
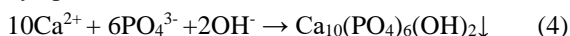


Figure 8. XRD of precipitate from the reaction of CaO, Ca(OH)₂ and KH₂PO₄ solution

It is indicated that CaCO₃ is less soluble in aqueous solution; Therefore, the removal of phosphate was based on adsorption process on the surface of this material [12]. On the other hand, the dissociation of Ca²⁺ ions from CaO and Ca(OH)₂ occurred easily in aqueous solution; Then these ions react with phosphate to form hydroxylapatite through precipitation. This process transferred phosphate from solution to precipitate. In aqueous solution, the reaction of calcium ions and phosphate solution to form hydroxylapatite is described as follows:



In fact, hydroxylapatite, a calcium phosphate mineral has been applied for plants as P-fertilizer [30]. Rock phosphate is a finite resource, and the shortage of phosphate fertilizer will threaten food supply in the future. Thus, hydroxylapatite formed from phosphate treatment can be a source of P-fertilizer supply for agriculture to solve the reduction of rock phosphate mining in nature.

Table 1 summarizes phosphate removal capacities by using a variety of materials from other researches. CaO and Ca(OH)₂ in this work has much higher phosphate removal capacities, compared to almost other materials. This comparison reveals that CaO and Ca(OH)₂ are the promising precipitants for efficient phosphate removal in aqueous solution. In order to achieve the effect of phosphate removal, there needs to prevent moisture to generate Ca(OH)₂ from CaO. Although phosphate removal capacity of CaCO₃ in this study is low, this value is still

higher than some materials listed in Table 1. Since this material is available and inexpensive, it could be applied for phosphate treatment at low concentration.

Table 1. Comparison of phosphate removal capacity to other different materials

Material	Q _{max} (mg/g)	Ref.
Commercial granular ferric hydroxide	105.0	[13]
Ferrihydrite	21.7	[14]
Iron oxide from red mud waste	12.9	[15]
Aluminium hydroxide gel	18-21	[16]
Commercial Lanthanum hydroxide	55.6	[17]
Calcite	6.0	[12]
CaCO ₃ -montmorillonite	0.3	[18]
Zeolite (from fly ash)	8.3	[19]
Ca(OH) ₂ -treated natural zeolite	8.8	[20]
Al-impregnated mesoporous silica	26.7	[21]
Mg-modified corn biochar	239.0	[22]
Ca-Mg loaded corncob biochar, 600°C pyrolysis	326.6	[23]
CaO-MgO-carbon composite	207.8	[24]
Fe-impregnated waste activated sludge biochar	111.0	[25]
Magnetic biochar from orange peel	1.2	[26]
Chitosan grafted quaternized resin	59.1	[27]
Chitosan-poly (ethyleneimine) double network cryogels	111.9	[28]
BOF slag	30.0	[29]
CaCO ₃	4.0	This work
CaO	287.4	This work
Ca(OH) ₂	235.2	This work

4. Conclusion

The removal of phosphate by using CaCO₃ could be applied in the range of low phosphate concentration. It is suggested that the potential application of CaO and Ca(OH)₂ for phosphate treatment can be extended in practice. The highest of phosphate removal capacity accounted for 287.36 mg/g and 235.21 mg/g at initial phosphate concentration of 500 ppm, and the phosphate removal efficiency was 85% and 97% at initial phosphate concentration of 5 ppm by using CaO and Ca(OH)₂, respectively. However, the filtration method should be improved or flocculant will be added to phosphate solution to increase phosphate removal capacity at initial concentrations of 50 and 1000 ppm in the future. Hydroxylapatite was found in the precipitate after chemical precipitation, and this product can be used as P-fertilizer for plants in acid crops. To conclude, the product after phosphate treatment can be used for agriculture and it is unnecessary to treat it as a secondary pollutant, compared to other chemical precipitation method using salts of iron or aluminum.

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