ENHANCED REMOVAL OF PHOSPHATE FROM WASTEWATER BY PRECIPITATION COUPLED WITH FLOCCULATION

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Abstract - Eco-friendly flocculants of alginic acid, $NaHCO_3$ and $CaCl_2.2H_2O$ with advantages of strong gelation characteristics were prepared for supporting the removal of phosphate in synthetic wastewater using CaO and $Ca(OH)_2$ as precipitants. The effects of weight ratios of each component in flocculants, dosage of flocculants and initial phosphate concentration were investigated through batch of experiments. The results showed excellent flocculation performance with the weight ratio of alginic acid:$NaHCO_3$ and $CaCl_2.2H_2O$ at 1:0.3:0.02 and the dosage of flocculants at 0.0050 g/25 mL of phosphate solution in the range of initial phosphate concentration from 50 to 1000 ppm. Comparing to the sample without flocculants, the phosphate removal efficiency using CaO and $Ca(OH)_2$ with the addition of flocculants increased from 19 and 20% to 97% at the initial phosphate concentration of 50 ppm, respectively by filtration of filter paper 2.7 μm.

Key words - Alginic acid; calium alginate; gel formation; flocculant; phosphate removal

1. Introduction

Phosphate is a vital element for the growth of algal and other biological organisms in the water bodies. The enrichment of phosphate in the water causes eutrophication, and its consequence involves the deterioration of water quality due to the abundant growth of plants and ecological unbalance of affected water resources. Eutrophication causes the depletion of dissolved oxygen, production of poisonous compounds to fishes and the generation of bad odour and taste [1-5].

The main sources of phosphate in wastewater are derived from leaching of the natural mineral deposits, agricultural wastewater (fertilizer leaching, aquaculture activities and livestock operation), municipal wastewater (human sewage, septic tanks, detergents, cleaning and stormwater runoff) and industrial wastewater (food and beverage processing effluents). Therefore, there are rising research attempts focused on the expansion of eutrophication prevention technology [6-9].

Typical phosphate removal techniques such as chemical and biological treatments have been broadly applied. Although, biological phosphate removal is a widely used method to reduce phosphate concentration in full-scale wastewater treatment plants, the drawbacks of this method are low reliability, stability and removal speed [10-12].

Chemical precipitation is a method that converts soluble phosphate to insoluble phosphate; as the result, phosphate precipitate can then be separated from the solution by different methods such as settling, filtration and centrifugation. The major commercial processes for phosphate treatment from wastewater effluents by chemical precipitation usually use salts of iron and aluminum [13-15]. However, the residues of iron and aluminum ions in the solution can adversely affect plants and human health [16].

In previous research, we developed phosphate removal by chemical precipitation method using CaO and $Ca(OH)_2$ with significantly high phosphate removal capacity. This value made up at 287.36 mg/g and 235.21 mg/g, respectively. Moreover, the product after phosphate treatment can be used as phosphate fertilizer for plants in acid crops [17]. Nevertheless, separation of the precipitate by filtration method (2.7 μm filter paper) seems not to be effective in the sample of initial phosphate concentration at 50 and 1000 ppm. In order to support the separation process of the precipitate from aqueous solution, flocculant should be added to combine suspended matter into bigger aggregates.
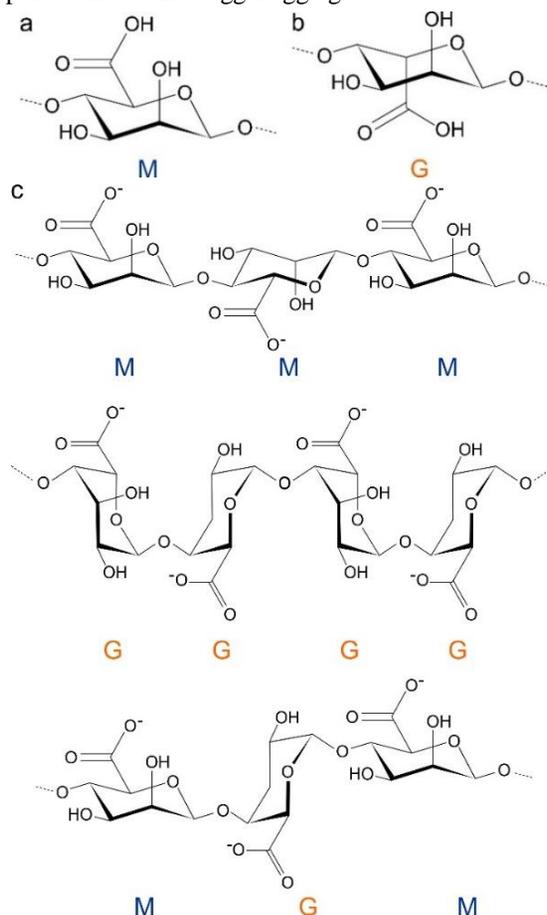
Figure 1. *(a) Chemical structure of mannuronic acid (M) and (b) guluronic acid (G) and (c) various chemical structures of the alginic acid components*

Alginic acid is a polysaccharide containing mannuronic acid (M) and guluronic acid (G) (Figure 1). This polymer chain can join each other in long sequences of M-blocks, G-blocks and MG-blocks [18-19]. Alginic acid is extracted from seagrass and brown seaweeds as dietary fibers [20]. Since alginic acid possesses characteristics of non-toxicity, biodegradability, stabilizing and gelling, it is used in medical and pharmaceutical applications, food industry, cosmetics and water purification as a stabilizer, emulsifier and humectant [21-22].

In this work, various flocculants for supporting the separation of phosphate precipitate by using the filtration method were investigated in detail through batch tests. The weight ratio of individual reagent in the flocculants and the dosage of flocculants were also tested to find out the optimal parameters. Phosphate removal capacity with and without flocculants using the filtration method was examined to evaluate the effectiveness of flocculants addition. The mechanism of the generation of flocculants in the form of gel to group suspended precipitate into aggregates was also discussed.

2. Experimental

2.1. Materials and reagents

KH_2PO_4 (potassium dihydrogen phosphate from Kanto, Japan was employed for the preparation of phosphate stock solution (PO_4^{3-}). Working solutions of various phosphate concentrations were prepared, as required, from the stock by consecutive dilution. CaO (calcium oxide), $Ca(OH)_2$ (calcium hydroxide), $NaHCO_3$ (sodium hydrogen carbonate) and $CaCl_2.2H_2O$ (calcium chloride dihydrate) were supplied from Kanto, Japan. Alginic acid was obtained from Trademark, Japan. Phosphorus standard solution (P 1000 ppm), $C_6H_8O_6$ (L(+)-Ascobic acid), $(NH_4)_6$ $Mo_7O_{24}.4H_2O$ (hexaammonium heptamolybdate tetrahydrate), sulfuric acid (H_2SO_4) were purchased from Kanto, Japan. $K_2Sb_2(C_4H_2O_6)_2.3H_2O$ (bis[(+)-tartrato] diantimonate (III) dipotassium trihydrate) was obtained from Fujifilm Wako, Japan. Whatman 50 filter paper (2.7 μm particle retention) was supplied from International Ltd. Maidstone, England and 0.2 μm membrane filter (Omniporehydrophilic PTFE) was obtained by Merck Millipore Ltd, Ireland. All aqueous solutions using Mili-Q water were collected from Direct-Q UV3, Merck Millipore. All chemicals were of analytical grade and used as received.

2.2. Batch of experiments

2.2.1. Flocculants of alginic acid and NaHCO₃

Synthetic wastewater with initial phosphate concentration of 1000 ppm was prepared by KH_2PO_4 and Mili-Q water. The chemical precipitation was achieved by the addition of 0.0250 g of CaO to 25 mL of KH_2PO_4 solution (P 1000 ppm). The weight of samples (readability 0.1 mg) was measured by balance ATX124, Shimadzu, Japan. To promote the deposit of particles in the solution, the mixture of alginic acid and $NaHCO_3$ as the flocculants (0.0075 g) with different weight ratios 1:0, 1:0.02, 1:0.1, 1:0.3 and 1:0.5 was added to the phosphate solution containing CaO. After magnetically stirring for 5 min, the mixture was settled for turbidity measurement by portable turbidity meter.

2.2.2. Flocculants of alginic acid, NaHCO₃ and CaCl₂.2H₂O

0.0250 g of CaO was added to 25 mL phosphate solution of 1000 ppm. Next, 0.0075 g of alginic acid, $NaHCO_3$ and $CaCl_2.2H_2O$ as the flocculants with a variety of weight ratios 1:0.3:0, 1:0.3:0.02, 1:0.3:0.1 and 1:0.3:0.5 were added to the KH_2PO_4 solution and CaO powder. The final mixture was magnetically stirred for 5 min and settled for turbidity measurement by portable turbidity meter.

2.2.3. Dosage of alginic acid, NaHCO₃ and CaCl₂.2H₂O with different initial phosphate concentration

0.0250 g of CaO was added to 25 mL of KH_2PO_4 solution with different phosphate concentrations (50, 500 and 1000 ppm). Then 0.0025 g, 0.0050 g, 0.0075 g and 0.0100 g of alginic acid, $NaHCO_3$ and $CaCl_2.2H_2O$ with weight ratio of 1:0.3:0.02 was added individually to phosphate solution and CaO powder. Finally, the mixture was magnetically stirred for 5 min and settled for turbidity measurement by portable turbidity meter.

2.2.4. Studies of phosphate removal

Batch phosphate removal studies were conducted by mixing 0.1 g of CaO or $Ca(OH)_2$ with 100 mL of phosphate solution at various initial phosphate concentrations (50, 100, 500 and 1000 ppm) in the polypropylene bottle. The contents in the bottles were shaken in the water bath at 25°C for 18 h. Afterwards, the samples were: i) Filtered through a filter paper 2.7 μm; ii) Filtered through a membrane filter 0.2 μm; iii) Transferred to the beaker 200 mL. The flocculants of alginic acid: $NaHCO_3$: $CaCl_2.2H_2O$ with the optimal weight ratio were poured into the solution. The mixture was magnetically stirred for 5 minutes and settled for 10 minutes; iv) Finally, and the supernatant was filtered through the filter paper 2.7 μm.

2.2.5. Analysis method

The phosphate concentration in the initial samples and in the filtrated samples was analyzed by molybdenum blue method with ascorbic acid using UV/VIS/NIR spectrophotometer V-570, Jasco, Japan. The determination of phosphate concentration was conducted at 880 nm wavelength which corresponds to the maximum absorbance. The same procedure was also employed with blank samples for each series of batch of experiments. Calibration curve from phosphorus standard solution was conducted in each experiment to collect accurate results. One of the calibration curves is given in Figure 2.
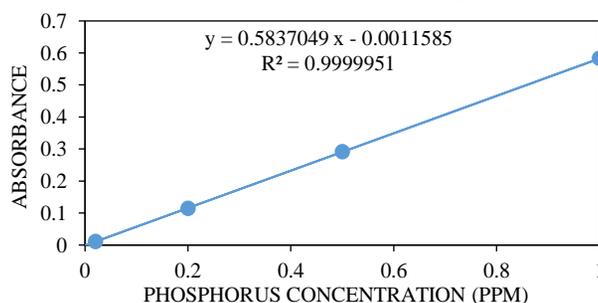

Figure 2. *Calibration curve of phosphorus standard solution at 880 nm*

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

$$H = \frac{C_0 - C_e}{C_0}.100\,(\%) \qquad (1)$$

$$q_e = \frac{C_0 - C_e}{M}.V \ (mg/g) \qquad (2)$$

Where, C_0 and C_e are the initial and equilibrium concentrations of phosphate (ppm), respectively, M is the mass of materials CaO or $Ca(OH)_2$ (g) and V is the volume of sample (L).

3. Results and discussion

3.1. Effect of alginic acid and NaHCO₃ as flocculants on phosphate separation

In previous work, the phosphate removal by using CaO and $Ca(OH)_2$ was tested at initial phosphate concentrations from 5 to 1000 ppm [17]. The results showed that the phosphate removal efficiency reached 85% and 95% at the initial phosphate concentration of 5 ppm by using CaO and $Ca(OH)_2$, respectively. However, the phosphate removal efficiency was only 19% and 20% at the initial phosphate concentration of 50 ppm, and 18% and 12% at the initial phosphate concentration of 1000 ppm by using CaO and $Ca(OH)_2$. These results suggested that the filter paper with pore size of 2.7 μm was not suitable for the capture of particles at initial phosphate concentration of 50 and 1000 ppm. Therefore, the addition of flocculants to combine suspended particles to become larger that can be separated easily from phosphate solution is investigated in this research.

Firstly, the flocculants of alginic acid and NaHCO₃ was tested with various weight ratios 1:0, 1:0.02, 1:0.1, 1:0.3 and 1:0.5. After pouring the flocculants into the phosphate solution containing CaO, the samples were magnetically stirred for 5 min then settled for turbidity measurement after each 300, 600, 900, 1200, 1500 and 1800 seconds. To benchmark the performance of alginic acid and NaHCO₃ with different weight ratios, the sample without flocculants was also investigated in the same condition. As found in Figure 3, the turbidity of all samples decreased with the increase of settling time and reached the lowest point at 58.8 NTU after 1800 seconds for all samples. The samples of alginic acid and NaHCO₃ with weight ratios of 1:0, 1:0.02 and 1:0.5 had turbidity higher than the sample without flocculant after settling from 300 to 1500 seconds. Nonetheless, the turbidity of the samples with weight ratios of 1:0.1 and 1:0.3 was lower than the sample without flocculants during the settling time from 300 to 1500 seconds. The increase of turbidity with the addition of alginic acid and NaHCO₃ with the weight ratio of 1:0 indicated that only alginic acid could not combine the suspended particles in the solution. The mixture of alginic acid and NaHCO₃ started effectively in the presence of NaHCO₃ with the rise of weight ratio from 0.02 to 0.3. However, the excess weight ratio of NaHCO₃ to 0.5 caused the increase of turbidity. Compared to the settling performance of the two samples 1:0.1 and 1:0.3, the weight ratio of 1:0.3 was better than 1:0.1; therefore, the mixture of alginic acid and NaHCO₃ with the weight ratio of 1:0.3 was selected for further experiments.
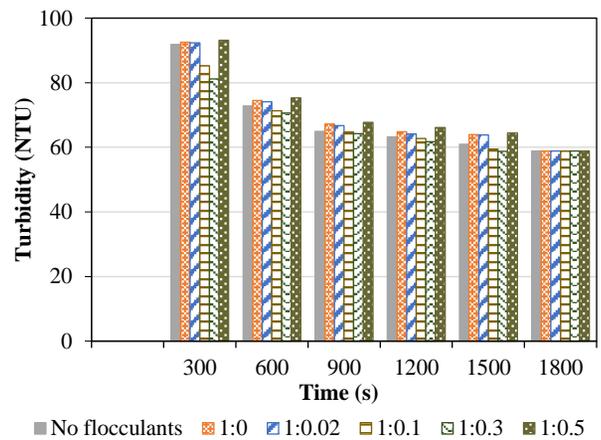
Figure 3. Effect of alginic acid and NaHCO₃ as flocculants with the different weight ratios on phosphate separation. Phosphate solution with concentration of 1000 ppm containing 0.0250 g of CaO

3.2. Effect of alginic acid, NaHCO₃ and CaCl₂.2H₂O as flocculants on phosphate separation

In order to improve the effectiveness of flocculants for the separation of phosphate precipitate, calcium chloride salt ($CaCl_2.2H_2O$) was added to the mixture of alginic acid and NaHCO₃. The weight ratios of alginic acid, NaHCO₃ and $CaCl_2.2H_2O$ was tested at 1:0.3:0, 1:0.3:0.02, 1:0.3:0.1 and 1:0.3:0.5. As seen in Figure 4, the turbidity of the sample with the weight ratio of 1:0.3:0.02 declined rapidly from 52.5 to 39.7 NTU after settling from 300 to 1800 seconds. Comparatively, the turbidity of the sample in the presence of $CaCl_2.2H_2O$ with the weight ratio of 1:0.3:0.02 after settling for 300 min (52.5 NTU) was lower than the sample with the weight ratio of 1:0.3:0 after settling for 1800 seconds (58.8 NTU). It was noted that the turbidity rose dramatically with the increase of weight ratio of $CaCl_2.2H_2O$ from 0.1 to 0.5. It was supposed that these two-weight ratios were not suitable which increased the suspended particles in the solution. Thus, the weight ratio of alginic acid, NaHCO₃ and $CaCl_2.2H_2O$ at 1:0.3:0.02 was chosen for the next experiments.
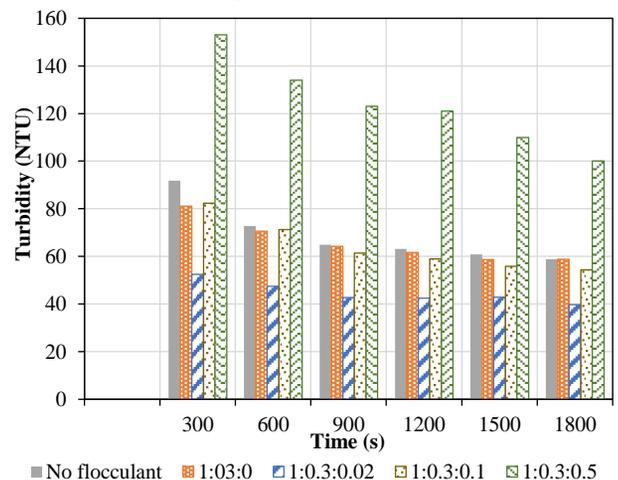
Figure 4. Effect of alginic acid, NaHCO₃ and CaCl₂.2H₂O as flocculants with the different weight ratios on phosphate separation. Phosphate solution with concentration of 1000 ppm containing 0.0250 g of CaO

3.3. Effect of dosage of alginic acid, NaHCO₃ and CaCl₂.2H₂O with different phosphate concentration on phosphate separation

To evaluate the performance of alginic acid, NaHCO₃ and CaCl₂.2H₂O dosage in the separation of precipitate, each 0.0025 g, 0.0050 g, 0.0075 g and 0.0100 g of flocculants with the weight ratio of 1:0.3:0.02 were added to the mixture of CaO and phosphate solution with various initial phosphate concentrations of 50, 500 and 1000 ppm. The effect of flocculants dosage on the separation of suspended matter is illustrated in Figure 5. The turbidity of all samples dropped significantly with the increase of flocculants dosage from 0.0025 to 0.0050 g. However, this value was increased substantially with the enhance of flocculants dosage from 0.0075 to 0.0100 g. The lowest turbidity was obtained at 7.2, 7.9 and 8.5 NTU with the flocculants dosage of 0.0050 g at initial phosphate concentration of 50, 500 and 1000 ppm, respectively. This amount of flocculants dosage was picked for further experiments.
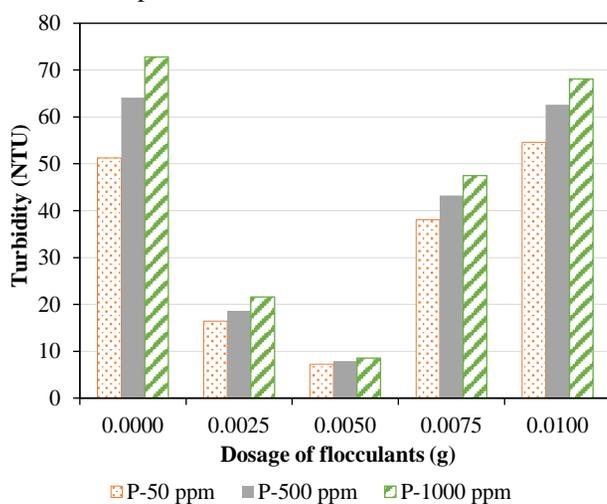

Figure 5. *Effect of dosage of alginic acid, NaHCO₃ and CaCl₂.2H₂O with various phosphate concentrations on phosphate separation*

3.4. Effect of alginic acid, NaHCO₃ and CaCl₂.2H₂O on phosphate removal by using CaO and Ca(OH)₂ as precipitates through filtration method

Figure 6 and Figure 7 show the phosphate removal capacity with the initial phosphate concentration from 50 to 1000 ppm by using CaO and Ca(OH)₂. Three different types of filtration including filter paper 2.7 μm without flocculants, membrane filter 0.2 μm without flocculants and filter paper 2.7 μm with flocculants were carried out to assess the performance of flocculants. The figures demonstrate that phosphate removal capacity by CaO and Ca(OH)₂ as precipitants using filtration of membrane filter 0.2 μm without flocculants was similar to filtration of filter paper 2.7 μm with the add flocculants in the range of the initial phosphate concentration from 50 to 100 ppm. Increasing the phosphate concentration between 500 and 1000 ppm, phosphate removal capacity using filtration of filter paper 2.7 μm with flocculants was much higher than the cased using filtration of membrane filter 0.2 μm without flocculants. Remarkably, the phosphate removal capacity by filtration through filter paper 2.7 μm with

flocculants was improved significantly, comparing to the filtration by filter paper 2.7 μm without flocculants. The phosphate removal capacity by filtration of filter paper 2.7 μm enhanced from 177.25 to 260.42 mg/g, and from 117.47 to 236.09 mg/g when flocculants were added to the phosphate solution of 1000 ppm in the presence of CaO and Ca(OH)₂, respectively.
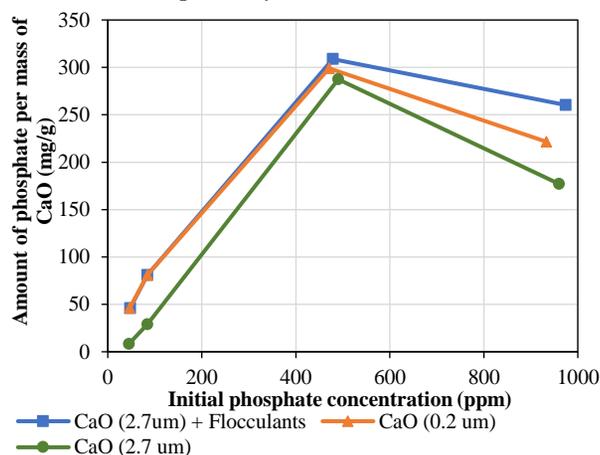

Figure 6. *Phosphate removal capacity by using CaO with different filtration with and without flocculants*

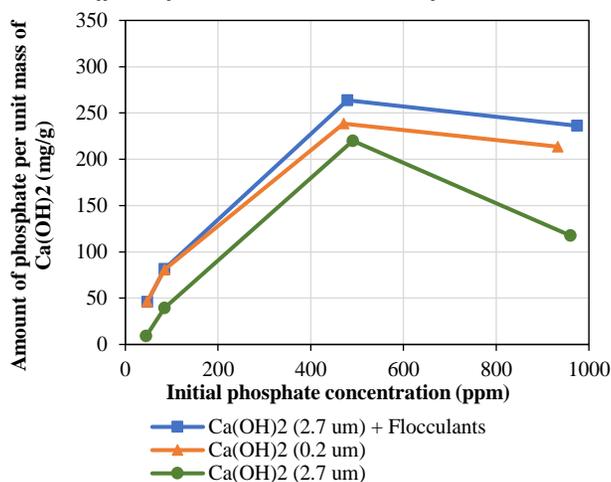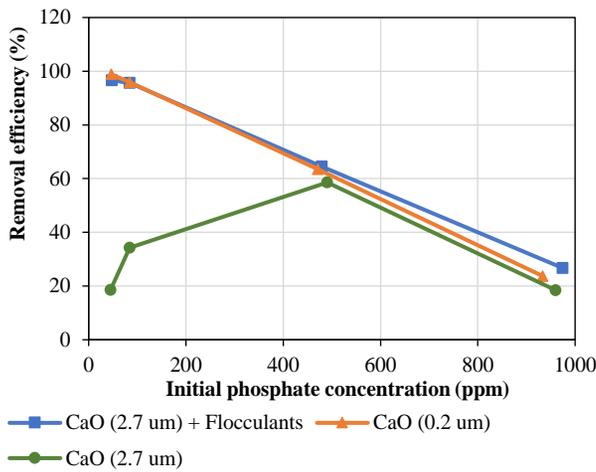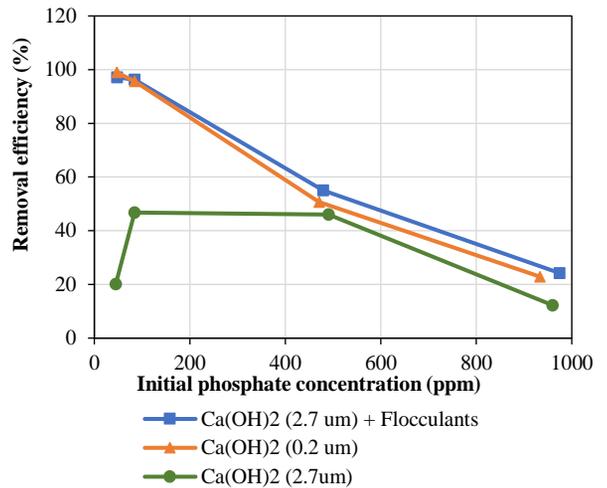**Figure 7.** *Phosphate removal capacity by using Ca(OH)₂ with different filtration with and without flocculants*

The phosphate removal efficiency by CaO and Ca(OH)₂ by three kinds of filtration are given in Figure 8 and Figure 9. Similar to the results of the phosphate removal capacity, phosphate removal efficiency by filtration of filter paper 2.7 μm without flocculants was considerably lower than the filtration of filter paper 2.7 μm with the addition of flocculants. In addition, using the same filter paper 2.7 μm, phosphate removal efficiency by CaO increased from 19 to 97% and from 34 to 96% with the addition of flocculants at the initial phosphate concentration of 50 and 100 ppm, respectively. Similar results using Ca(OH)₂ were also recorded with phosphate removal efficiency rose from 20 to 97% and from 47 to 96% with the presence of flocculants at the initial phosphate concentration of 50 and 100 ppm. All the results strongly confirmed that alginic acid, NaHCO₃ and CaCl₂.2H₂O as flocculants played a crucial role to combine the suspended particles in the solution to form the bigger size for easier separation.

Figure 8. *Phosphate removal efficiency by using CaO with different filtration with and without flocculants*

Figure 9. *Phosphate removal efficiency by using Ca(OH)$_2$ with different filtration with and without flocculants*
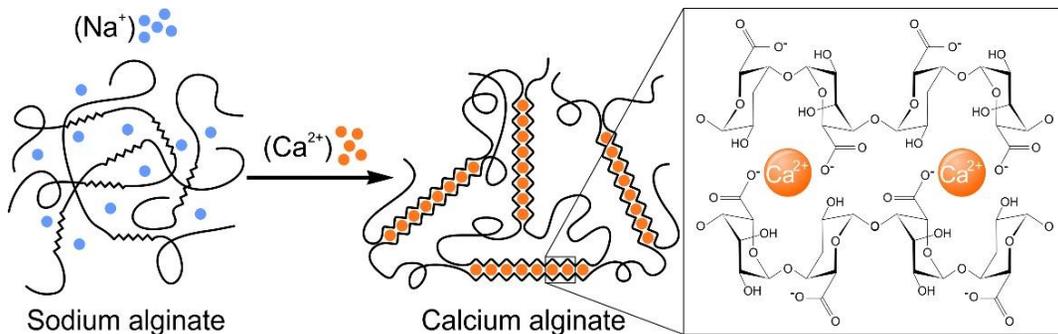
Figure 10. *The formation of calcium alginate and the structure of the "egg-box" model. Reproduction from [24]*

3.5. *Mechanism of flocculants formation form for phosphate precipitates separation*

The chemical reaction of alginic acid and NaHCO$_3$ leads to the formation of sodium alginate. This compound produces a highly viscous aqueous solution. However, sodium alginate only increases viscosity. In the presence of bivalent cations, especially Ca^{2+}, they generate strong gels. Calcium alginate gelation occurs when Ca^{2+} interact ionically with blocks of gluronic acid (G-blocks), resulting in the generation of the three-dimentional network through physical crosslink or connecting bridges [23-24]. This change arrangement is often described as the "egg-box" model. The formation of calcium alginate and the structure of "egg-box" is illustrated in Figure 10. Due to the formation of strong calcium alginate gels, the large aggregation of suspended particles can be formed and be separated later by the filtration method. As the result, the phosphate removal rate increased significantly by the filtration of filter paper 2.7 μm with the addition of alginic acid, NaHCO$_3$ and CaCl$_2$.2H$_2$O.

4. Conclusion

The mixture of alginic acid, NaHCO$_3$ and CaCl$_2$.2H$_2$O exhibited promising flocculants for separation of suspended phosphate precipitates and improvement of phosphate removal from aqueous solution. According to the gelation properties of flocculants, the phosphate removal capacity and phosphate removal efficiency by CaO and Ca(OH)$_2$ as precipitants using filtration of filter

paper 2.7 μm rose dramatically in the range of initial phosphate concentration from 50 to 1000 ppm, comparing to the filtration with the same pore size of filter paper without flocculants.

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