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Preliminary study of calcium silicate hydrate (tobermorite) as crystal material to recovery phosphate from wastewater

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ABSTRACT

Phosphorus is an essential nutrient for the growth of organism and plays a key role in the health and functioning of both terrestrial and aquatic ecosystems. However, excessive amounts of phosphorus may lead to adverse effects on both the ecology and receiving waters. High phosphorus concentration is often associated with algal blooms which results in eutrophication. Therefore, phosphorus removal from water is essential to control the eutrophication. On the other hand, the demand of phosphorus resources for the production of fertilizer is growing. With the depletion of high-quality commercial phosphate rocks and the adoption of stringent phosphorus discharge limit of wastewater, phosphorus recovery from wastewater has become of great concern. A crystallisation process for recovering phosphates was developed using an artificial seed crystal material consisting of calcium silicate hydrate. Laboratory experiments were conducted to apply the seed material in the phosphorus recovery from both model water and sewage from a wastewater treatment plant. Literature reviews show that a normal crystallisation of phosphorus from wastewater needs a preliminary degassing of CO_2 from the wastewater. However, this process by using the developed seed required no pre-degassing process. In the treatment of model water with phosphate concentration of 30 mg/l, the phosphorus removal rate was 98%. The phosphate removal percentage with the seed materials was maintained at about 80% even the seed was reused by seven times. In the treatment of sewage with phosphate concentration of 20 mg/l and COD concentrations of 597 mg/l, phosphorus removal efficiencies with the seed ranged from 82% to 87%.

Keywords: Calcium silicate hydrate (Tobermorite); Crystallisation; Phosphate recovery; Sustainable reuse of resources

1. Introduction

Phosphorus will stimulate the growth of phytoplankton and aquatic plants. However, if an excess of phosphate enters the lake or surface water ecosystem, algae and aquatic plants will grow rapidly, choke up the waterway and use up large amounts of oxygen. This is known as eutrophication, which has been defined as "the enrichment of water by nutrients especially compounds of nitrogen and phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce and undesirable disturbance to the balance of organisms and the quality of the water concerned" [1].

The excessive inputs, usually a result of human activity and development, appear to cause an imbalance in the "production versus consumption" of living material (biomass) in an ecosystem. The system then reacts by producing more phytoplankton/vegetation than can be consumed

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by ecosystem. This overproduction can lead to a variety of problems ranging from anoxic waters (through decomposition) to toxic algal blooms and decrease in diversity, food supply and habitat destruction. Eutrophication as a water quality issue has had a high profile since the late 1980s [2], following the widespread occurrence of blue-green algal blooms in some fresh waters. Some blue-green algae can at times produce toxins, which are harmful to humans, pets and farm animals.

A number of international and national policy and strategies have been introduced to overcome the eutrophication problems. Urban waste water treatment directive [1] was adopted on the treatment of urban waste water in 1991. It is concerned with the collection, treatment and discharge of urban and certain industrial wastewaters, and addresses the waters suffering, or at risk from eutrophication. The directive sets minimum standards for the collection, treatment and discharge of urban waste water. The data refer to the size of the agglomeration (stated as sewage load in population equivalents (p.e.)) and the required discharge consents for phosphrous; 2 mg Pl^{-1} for 10,000–100,000 p.e. and 1 mg Pl^{-1} for more than 100,000 p.e.

Although significant progress has been achieved through the urban waste water directive, it has not achieved all of its stated goals. Given the increasing demand for cleaner water environments, the European parliament and council adopted a comprehensive water framework directive that entered into force on 22 December 2000 [3]. It requires all member states to adopt the directive into their national and regional water laws by December 2003. The purpose of the directive is to establish a framework for the protection of inland surface waters (rivers and lakes), transitional waters (estuaries), coastal waters and groundwater. It will ensure all aquatic ecosystems and, with regard to their water needs, terrestrial ecosystems and wetlands meet 'good ecological status' by 2015. For surface waters, the definition of 'good ecological status' means in terms of eutrophication.

Phosphorus recovery by crystallization process has been developed as an alternative technology for chemical precipitation process in wastewater treatment process. The advantages of crystallization process are the phosphorus can be recovered in usable products for recycling and that sludge generation from coagulant in the sewage treatment plants is reduced.

The most developed crystallization pathways at present are struvite (magnesium ammonium phosphate) and hydroxyapatite (HAP, calcium phosphate). A variety of seed crystal materials such as waste lime, converter slag, coal fly ash, sands and calcite have been investigated because the crystallization yield is affected by the seed material as well as pH value [4].

A full scale trial was performed in Netherlands applying sand as seed. But the process had the disadvantage that the dissolved carbon dioxide in water has to be removed prior to the crystallization step. This is affected by acidifying the water with sulphuric acid to pH ≈ 4.2 and stripping with air. The crystallization is then carried out after another pH adjustment to pH ≈ 9.0 with NaOH. This obviously consumes a lot of chemicals and correspondingly increase the cost of the technology.

Calcite and related materials were also previously investigated and lead to application in the waste water field [5]. But in all cases a pH ≈ 9.0 had to be applied for a sufficient phosphorus retention which does not suit ecosystems such as catchments and lakes. Waste lime as seed material was studied in Korea. This lime contains 60% cations (mainly calcium, some magnesium, small amounts of iron, aluminium). High pH was also applied to the study.

The aim of this study is to investigate an effective and economical seed material to recover phosphate from real wastewater via calcium phosphate crystallisation.

2. Experimental methods

2.1. Chemicals

Tobermorite have been studied as seed material for crystallization of calcium phosphate from municipal wastewater [6,7]. It is one of the crystal forms of the calcium silicate hydrate. The molecular formula of the tobermorite is written as $5CaO\cdot6SiO_2\cdot5H_2O$. The pellet of seed material (tobermorite-like) was synthesized and the chemicals used were $Na_2Si_3O_7$, $NaH_2PO_4\cdot H_2O$, (98.0–102.0%), both were provide by Sigma-Aldrich, UK; $CaCl_2\cdot2H_2O$, (99%), NaOH, (98+%) and sulphuric acid (98%) were provided by the Fisher, UK.

A 0.02 M solution of $Na_2Si_3O_7$ (300 ml) was mixed with 0.05 M $CaCl_2\cdot2H_2O$ (100 ml), to give a Ca/Si ratio of 5/6 (tobermorite composition). A 0.05 M NaOH solution (200 ml) was added dropwise (20 ml l^{-1}) to the mixture of $Na_2Si_3O_7$ and $CaCl_2\cdot2H_2O$ solutions over 10 h by a peristaltic pump. The white precipitate and supernatant were aged at room temperature for seven days in a polypropylene bottle. The resultant precipitate in the bottle was separated by centrifugation and then washed by redispersing it in deionized water and separation by centrifugation. This procedure was repeated until the supernatant was free from chloride ions as determined using $AgNO_3$. Finally, the precipitate was spread on a glass slide and dried in oven at 104°C overnight.

2.2. Model water study

Preparation 2 g l^{-1} stock solution $NaH_2PO_4\cdot H_2O$ as PO_4^{3-}. Dissolve 2.91 g $NaH_2PO_4\cdot H_2O$ in one liter distilled water. 1.5 ml of 2 g l^{-1} $NaH_2PO_4\cdot H_2O$ solution was mixed with 98.5 ml distilled water to reach 30 mg l^{-1}

$NaH_2PO_4 \cdot H_2O$ as PO_4^{3-} in a plastic bottle, calcium chloride was added to the solution, and then the solution was shaken in a temperature controlling shaker at a speed of 203 revolutions per min and a room temperature of 25 ± 0.5°C for 30 min. The seed material was then added into the solution. A further three hours mixing was applied at the same speed and the same temperature to make the seed completely mixed with the synthesis solution; afterwards, it was changed to a slow mixing at a speed of 60 rpm for one hour followed by 30 min settlement period.

The solutions were filtered by 0.45 µm membrane (Millipore). pH was measured by pH meter. Phosphate concentration was measured by the ascorbic acid method [8] with a spectrophotometer at the wavelength of 880 nm.

2.3. Real sewage study

The sewage was taken from a sewage treatment work. The sample point was before pre-sedimentation. The concentration of phosphate, the COD and the pH were measured immediately after the samples were taken and brought into the laboratory. The characteristics of the sewage are shown in Table 1, where the data shown were in average with the standard deviation of ±5%. The phosphate removal study with real sewage was performed following the same procedures as detailed above. The quality parameters were measured following the same standard methods [8].

Table 1
Quality characteristics of sewage

COD (mg l^{-1})	597
pH	6.8
Phosphate (mg l^{-1})	20.2
BOD (mg l^{-1})	200
Suspended solids (mg l^{-1})	578

3. Results and discussion

3.1. The properties of the seeds

The composition of the synthesised seed was analysed by a Philips PW 1480 X-Ray fluorescence spectrometer, with a dual anode Sc/Mo 100 kV 3 kW X-Ray tube. The spectrometer is calibrated and the samples measured using Philips X40 analytical software. The major elements were CaO (42.03%) and SiO_2 (12.47%). The density of the seed material is between 0.332–1.018 g cm^{-3}, depending on the ratio of Ca to Si. The high Si strength results in high density of calcium silicate hydrate.

The scanned electronic microscope measurements were carried out to measure the product size. The effect of the ratio of Ca to Si on the particle size of the resulting products can be seen in Fig. 1. Increasing Si strength up to 1:5 as Ca to Si ratio increases the particle size significantly, from 5–10 µm to 40–50 µm, but further increasing

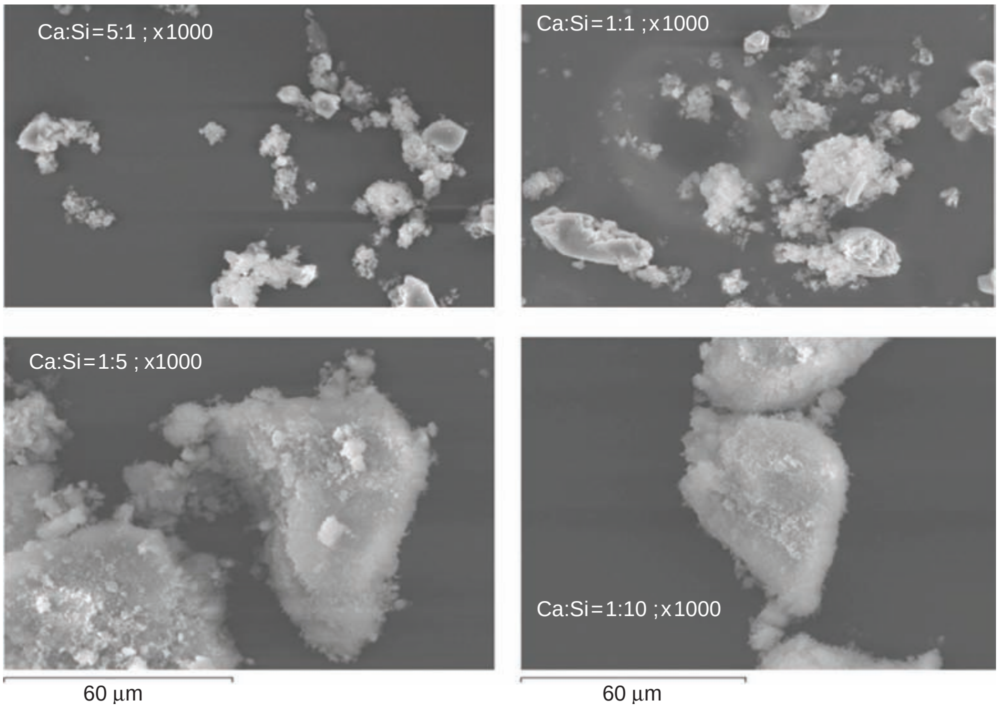

Fig. 1. The image of calcium silicate hydrate: the effect of Ca:Si ratio on the product size.

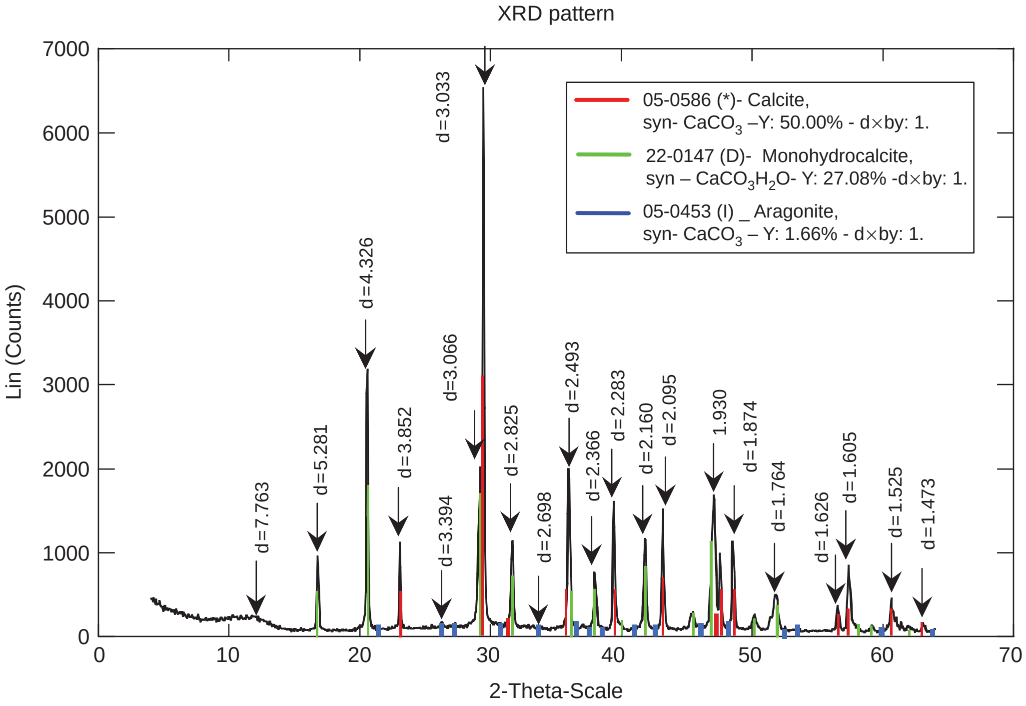

Fig. 2. The XRD pattern of calcium silicate hydrate material.

Si, e.g., Ca:Si ratio to 1:10, would not have greater size than that with 1:5 Ca:Si.

The X-ray diffraction (XRD) pattern can be seen in Fig. 2, which was obtained for randomly orientated samples using a Siemens D5000 diffraction system and the data was processed using Siemens Diffrac Plus processing software. The major elements of the seed are calcite and monohydrocalcite.

3.2. Effects of Ca/P on the phosphate removal

In order to study the effect of the dose of $CaCl_2$ on the phosphate removal, model water with phosphate concentration of 30 mg l^{-1} was prepared. The model water was mixed with various doses of $CaCl_2$ in the presence of calcium silicate hydrate with a dose of 5 g l^{-1} following the procedures detailed before. The phosphate removal efficiency is plotted with respect to the Ca/P molar ratio in Fig. 3.

In this experiment, Ca:P molar ratio ranged from 1 to 16. From Fig. 3, phosphate removal increased with increasing quantities of calcium. The maximum removal rate (93.9%) was reached at Ca:P molar ratio 15. However, 90.5% of phosphate removal rate was achieved without dosing any CaCl2 but with 5 g l^{-1} calcium silicate hydrate alone, indicating the resulting product used is a good material for the phosphate removal.

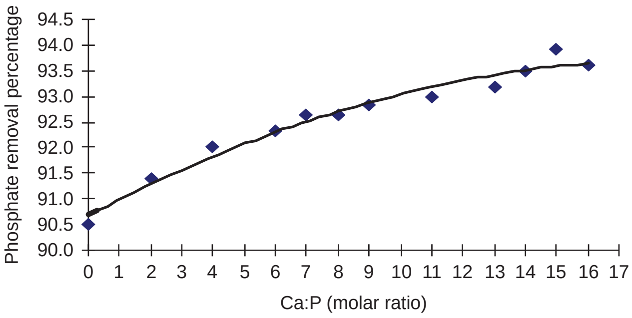

Fig. 3. Effect of calcium on phosphate removal.

3.3. Effect of the ratio of Ca:Si on the phosphate removal

It was found that the ratio of Ca:Si in calcium silicate hydrate affects the P removal. As can be seen in Fig. 4, that when Ca:Si was up to 1:5, the percentage removal of P reached to a high level of greater than 95% for a wide dose range, increasing Si contents further dose not significantly achieve more P removal. And also, the P removal with calcium silicate hydrate at Ca:Si of 1:1 was the lowest in comparison with that by all other Ca:Si ratio products. The observed results could be attributed to that when the ratio of Ca:Si was 1:5, the inter-layer of the material was expanded which could take more phosphate than other materials with various Ca:Si ratios. The evidence of this

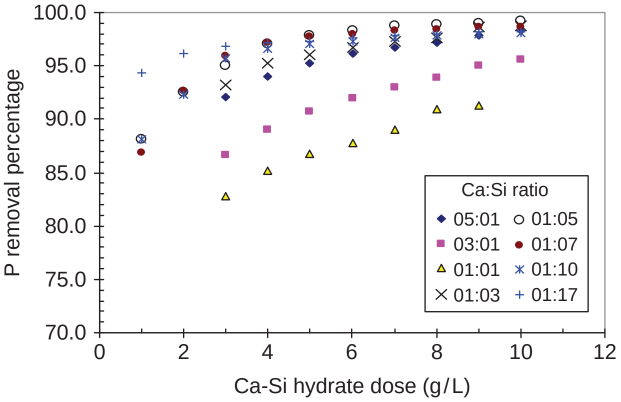

Fig. 4. Effect of the ratio of Ca:Si in calcium silicate hydrate on phosphate removal.

was that a relatively overall particle size (Fig. 1) and larger basal spacing (Fig. 2) of the materials with Ca:Si ratio of 1:5.

From Fig. 4, it can also be seen that with increasing the dose of calcium silicate hydrate, the phosphate removal efficiency increased for all Ca:Si ratio products. It shows that by adding 0.4 g l^{-1} material, the phosphate removal efficiency can reach 97.5% if the Ca:Si ratios were above 1:5. Therefore, the dose of 0.4 g l^{-1} was taken for further studies.

3.4. Effectiveness of the used calcium silicate hydrate

After the first time use, the calcium silicate hydrate was oven-dried at 104°C and then reused in the experiments. The results are shown in Table 2. The materials was reused seven times. It shows that without any regeneration procedure, the maximum phosphate elimination rate can reach 98.2%. The phosphate removal rate was decreased from 98.4% to 85.4% after seven times.

3.5. Phosphate removal from raw sewage

3.5.1. The effect of calcium silicate hydrate dose on phosphate removal

Different doses of calcium silicate hydrate were weighed and added to 100 ml sewage, 3 h fast shaking (rpm = 203), 1 h slow shaking (rpm = 50), and 1 h sedimentation were applied. Afterwards, water samples were withdrawn and the phosphate concentration was measured.

The effect of calcium silicate hydrate dose on phosphate percentage removal is shown in Table 3. It can be seen that for the dose of 4 g l^{-1}, phosphate removal efficiency was about 82.5%.

Although the dose of 6 g l^{-1} can achieve the highest P removal efficiency, but the residual COD and BOD were higher than that by other doses. Compare to the dose 6 g l^{-1}, the dose of 5 g l^{-1} can achieve the similar removal efficiency of P but much better COD and BOD removal, then the dose of 5 g l^{-1} was determined to use as optimum dose for the real sewage treatment.

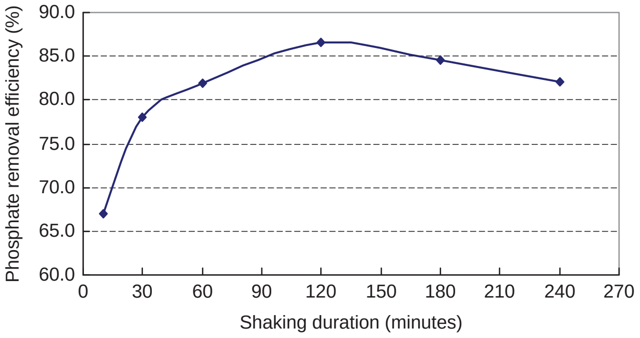

Fig. 5. Phosphate removal as a function of shaking duration.

Table 2
The results of reusing calcium silicate hydrate for seven times

Trial	1	2	3	4	5	6	7
Dose (g l^{-1})				4			
Final pH	10.2	9.94	9.88	9.64	9.14	8.74	8.56
Remaining phosphate (mg l^{-1})	0.469	1.671	1.853	0.53	1.628	3.977	4.372
Removal efficiency (%)	98.4	94.4	93.8	98.2	94.6	86.7	85.4

Table 3
The effect of Ca–Si hydrate dose on P removal and the treated sewage quality

Seed dose (g l^{-1})	Final pH	COD (mg l^{-1})	BOD (mg l^{-1})	Suspended solids (g l^{-1})	Phosphate removal efficiency (%)
4	8.65	111	87.86	4.036	82.5
5	8.76	136	71.67	4.996	86.4
6	8.81	160	128.33	5.922	87.5

Table 4
The effect of initial pH

Seed dose g (100 ml)$^{-1}$	Initial pH	Final pH	Suspended solids (gl^{-1})	Removal efficiency (%)
0.5	6	8.71	4.869	87.4
0.5	7	8.80	4.996	86.4
0.5	8	9.04	5.017	86.4
0.5	9	9.27	5.230	85.3

3.5.2. The effect of shaking period on phosphate removal

Different shaking duration (from 10 min to 240 min) was applied. Ca–Si hydrate dose was fixed to 5 gl^{-1}, shaking speed was 203 rpm. Water samples were withdrawn and the phosphate concentration was measured. The maximum phosphate removal (86%) was achieved at 120 min shaking (Fig. 5).

3.5.3. The effect of initial pH

Initial pH of sewage was adjusted to 6, 7, 8, and 9 by 1 M NaOH or 1 M HCl. 5 gl^{-1} of Ca–Si hydrate was mixed with sewage. After 3 h shaking, water samples were withdrawn and the phosphate concentration was measured. An example of the effect of initial pHs on phosphate removal is shown in Table 4. The original sewage pH was 6.8, there is no great different on phosphate removal by changing the pH value. So it's not necessary to adjust the initial pH.

4. Conclusions

The developed calcium silicate hydrate was demonstrated to be effective in the phosphate removal without the need of dosing extra $CaCl_2$. The P removal by Ca–Si hydrate is affected by the nature of crystal, phosphate concentration, Ca:Si ratio and the material dose. From the first study using model water, the phosphorus removal percentage reached as high as 98%, even after seven times reuse, the Ca–Si hydrate material still can achieve around 80% phosphate removal. When applied to sewage with a phosphate concentration of 20 mg l^{-1}, the phosphorus removal percentage was more than 80%.

Future work is suggested to investigate the effect of temperature on the phosphorus removal, the modification and regeneration conditions to improve phosphate removal efficiency from sewage and the effect of regeneration time, temperature on the performance of regenerated materials. The comparative cost of the phosphate recovery by calcium–silicate phosphate crystallisation should be studied. Finally, the environmental/risk assessment of the disposal of used Ca–Si hydrate also should be conducted.

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