Recovery of Phosphate from Surface Waters Using a Calcium Silicate Composite Material for Potential Application in Environmental Remediation

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ABSTRACT

We report on the use of a high surface area calcium silicate material (Nanostructured Calcium Silicate, NCaSil) as an adsorbent for phosphate at concentrations typically observed in polluted surface waters (0.3 mg P dm^{-3}). The material exhibits a high degree of phosphate uptake (> 87%) when applied to contaminated waters at a loading of at least 0.25 g dm^{-3}. The NCaSil can be prepared with a Ca:Si ratio in excess of 1:1 in order to improve the phosphate uptake capacity. We further demonstrate the use of the silicate material in a continuous adsorption set-up, or via the preparation of a composite material containing magnetic centers to facilitate separation of the sorbent after use. Finally, we demonstrate the use of NCaSil as an adsorbent for the remediation of phosphate-contaminated surface waters.

Keywords: calcium silicate, environmental remediation, phosphate

1 INTRODUCTION

Eutrophication of lowland water sources, especially lakes, due to contamination by phosphate-containing run-off from agricultural activities is a major environmental concern. Successful remediation of the polluted water sources can be problematic due to the low concentration of phosphate in the contaminated water (< 1 mg P dm^{-3}). There are two strategies commonly employed for this purpose. The first strategy is to contain the phosphate within the sediment of the polluted water source, and thus, limit its bioavailability. Materials used for this purpose typically include a high content of aluminum, calcium or iron, and act by forming highly insoluble phosphate minerals [1-2]. One notable commercial example of this is Phoslock®, a lanthanum-modified clay [3]. These materials are designed to remain in permanent contact with the water source, so must be intrinsically non-hazardous. Another strategy often investigated for the remediation of phosphate from polluted surface waters is separation and recovery of the adsorbent, for example, magnetic separation of an iron-containing adsorbent [4]. The advantage of this technique is that the adsorbent material may be regenerated and recycled, with potential recovery of the phosphate for commercial gain.

We have developed a nanostructured calcium silicate material (NCaSil), which consists of small nano-scale platelets randomly arranged into particles of a few microns in diameter. This imparts to the material a large surface area of up to 600 m^2 g^{-1}, with chemically active calcium and hydroxyl ions at the surface of the platelets [5]. The chemical reactivity of NCaSil makes it suitable as an adsorbent for a variety of pollutant materials [6-7]. However, the small particle size, and large surface area of the material means large-scale separation of NCaSil from suspension is problematic as the particles have a slow settling rate, and the thixotropic nature of the NCaSil filter cake leads to slow filtration rates.

Previous studies with NCaSil [8-9], using concentrated phosphate solutions (30 mg P dm^{-3} – 3 g P dm^{-3}) have demonstrated that the material has a large affinity for phosphate, being capable of adsorbing up to 6 wt.% P, with the adsorption process exhibiting second order kinetics. The adsorption occurs via a two-step mechanism, where the NCaSil initially reacts with H$^+$, resulting in a positively charged intermediate species. This positively charged species then reacts with any phosphate present. As such, the adsorption of H$_2$PO$_4^-$ proceeds more rapidly than that of HPO$_4^{2-}$ or PO$_4^{3-}$ [8]. When exposed to concentrated phosphate solution, the reaction with NCaSil leads to the formation of the brushite phase, CaHPO$_4$.2H$_2$O [9].

In this paper, we extend the studies of phosphate adsorption by NCaSil to concentrations typically encountered in polluted surface waters (0.3 mg P dm^{-3}), and demonstrate strategies by which the separation and recovery of the adsorbent may be achieved. This is done by the incorporation of magnetic centers within the NCaSil structure, improving its flocculation characteristics. Adsorption studies on samples of polluted surface waters are also presented.

2 EXPERIMENTAL

Calcium silicate (NCaSil) was prepared according to the method described by Johnston et al. [5], wherein a sodium silicate solution is added to a suspension of Ca(OH)$_2$ under vigorous mixing at a pH value of 11. This results in a precipitate with a median particle diameter of 19 µm and a chemical composition of (CaO)$_{0.8}$SiO$_{(2-x)}$(OH)$_{2x}$, (x < 0.5). Samples were also made in with an increased Ca:Si ratio, of up to 1.5:1. Unless otherwise specified, the ratio of Ca:Si in

the as-made NCaSil was fixed at 0.8:1. Magnetic Fe_3O_4-NCaSil composites were likewise prepared by pre-dispersing magnetite powder in the sodium silicate solution prior to its addition to the calcium hydroxide. A composite material containing 25 wt.% Fe_3O_4 was prepared.

Total reactive phosphate was quantified colormetrically using the molybdenum blue method [10]. Dissolved reactive phosphate was determined using the same technique, with the samples filtered through a 0.45 μm filter membrane before analysis. Dissolved silica was quantified colormetrically as the silicomolybdic acid complex [10]. Dissolved calcium was quantified by flame atomic absorption analysis using a Thermo Scientific iCE 3500 instrument.

For laboratory batch adsorption testing, phosphate solutions were prepared from KH_2PO_4 at a concentration of 0.3 mg P dm^{-3}. Batch adsorption tests were conducted by suspending an appropriate portion of the NCaSil material in 10 dm^3 of the phosphate solution circulated by means of an overhead stirrer operated at 300 rpm. Samples were withdrawn by syringe and immediately filtered through a 0.45 μm membrane. After the completion of the adsorption test, the NCaSil material was recovered by filtration.

Long-term stability tests were conducted by suspending a known mass of NCaSil in a 15 cm depth of 0.3 mg P dm^{-3} solution in a clear transparent glass bottle. The bottles were left sealed except during sampling, and were maintained at 20 °C during the adsorption tests.

Tests were also conducted with a packed radial flow cartridge (containing 3.5 g sorbent) suspended in 10 dm^3 of 0.3 mg P dm^{-3} solution, providing a NCaSil loading of 0.35 g dm^{-3}. The phosphate-containing solution was pumped through the cartridge at a rate of 250 cm^3 min^{-1}. This provided a flow linear flow rate of 4 cm min^{-1} through the adsorbent material.

Phosphate adsorption tests were conducted with the Fe_3O_4-NCaSil composite using a fluidized-bed arrangement. Phosphate solution (31 mg P dm^{-3}) was pumped upward through a 50 cm^3 (2 cm i.d.) glass column at a flow rate of 12.4 cm^3 min^{-1}, providing an upward velocity of 3.9 cm^{-1} min. The Fe_3O_4-NCaSil was used at a loading of 0.25 g per dm^3 of influent.

Samples of surface water were obtained from Lake Horowhenua in January 2013. The lake is a shallow lowland lake located at 40.61° S, 175.26° E, near Levin, New Zealand. The total reactive phosphate concentration of this water was determined as 0.28 mg P dm^{-3}, the dissolved reactive phosphate was determined to be 0.18 mg P dm^{-3}, and the pH determined as 9.0. Absorption tests with the NCaSil materials were commenced on the filtered water within 24 hours of collecting the water samples.

3 RESULTS

3.1 Batch Adsorption

The removal of phosphate from 0.3 mg P dm^{-3} solution by NCaSil samples with increasing Ca:Si ratios is shown in Figure 1. As a result of increasing the calcium content in the adsorbent material, an increased removal of phosphate from the solution is observed. This phosphate removal also proceeds more rapidly, resulting in a phosphate removal of 87% with 10 minutes of contact time by an adsorbent having a Ca:Si ratio of 1.5:1.
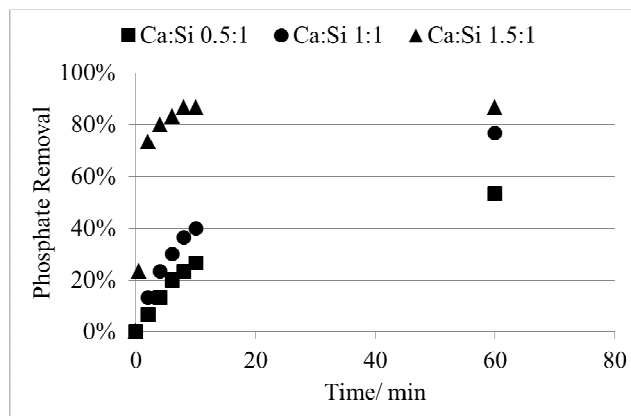

Figure 1: Phosphate removal from 0.3 mg P dm^{-3} solution by NCaSil with varying Ca:Si ratios at a loading of 0.25 g dm^{-3}.

3.2 Continuous Adsorption

Evaluation of the NCaSil in a radial flow column was carried out, the results of which are shown in Figure 2. It can be seen that the phosphate removal occurs at a slower rate than that observed in the batch adsorption experiment with the Ca:Si = 1:1 NCaSil shown in Figure 1. Phosphate removal of 43% was observed after 3 hours in the radial flow column, compared to a 77% removal after 60 minutes in the batch adsorption test. This is a total phosphate loading of 0.5 mg P g^{-1} NCaSil.

Release of calcium and silica into solution was observed in both the batch and continuous adsorption tests. An increase in the solution pH was also observed in conjunction with this calcium release. The final pH of 10.2 was observed during these tests, increasing from an initial pH of 5.4. This is associated with the dissolution of the NCaSil adsorbent, which is known to occur when the NCaSil is in contact with water [6], although it does not occur to the same extent when the NCaSil is in contact with concentrated phosphate solutions [8].
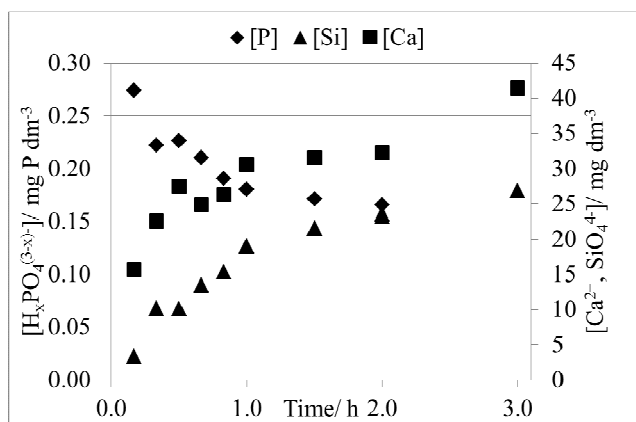
Figure 2: Uptake of phosphate by NCaSil in a radial flow cartridge. NCaSil applied at a loading of 0.35 g dm^{-3}.

Testing with a Fe_3O_4-NCaSil composite material in a continuous uptake system is shown in Figure 3. The material reaches saturation after 22 reactor volumes, at which point the spent material has a phosphate loading of 1 wt.% P. The total adsorbent loading used was 0.25 g per dm^3 of effluent volume. When testing was continued in excess of 22 reactor volumes, excess phosphate was leached from the composite material within the column.
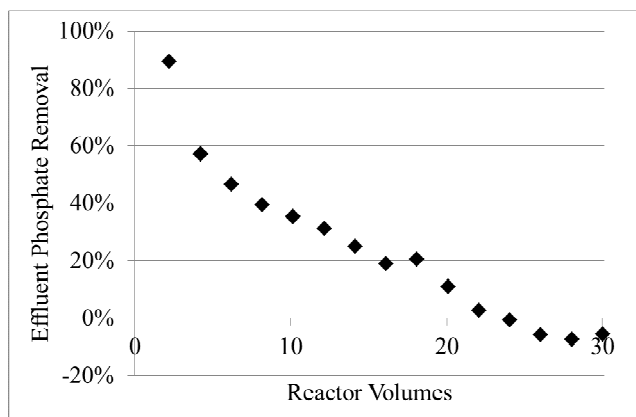

Figure 3: Removal of phosphate by Fe_3O_4-NCaSil composite from 31 mg P dm^{-3} solution in a fluidized bed column. Fe_3O_4-NCaSil applied at a total loading of 0.25 g per dm^3 effluent.

3.3 Long-term Stability

The long term stability of the NCaSil material in static contact with a phosphate solution was evaluated at different adsorbent loadings. The results, given in Figure 4, show that after 9 days, all samples exhibited a phosphate removal of greater than 85%. However, after 40 days, only the sample with an NCaSil loading of 0.5 g dm^{-3} retained this low phosphate removal. This is most likely due to the diffusion of atmospheric carbon dioxide into the test solutions. This would cause a decrease in the pH of the solution, thereby decreasing the stability of the NCaSil-

phosphate complex. This is further confirmed by the 40-day solution pH of these and other samples, shown in Table 1.
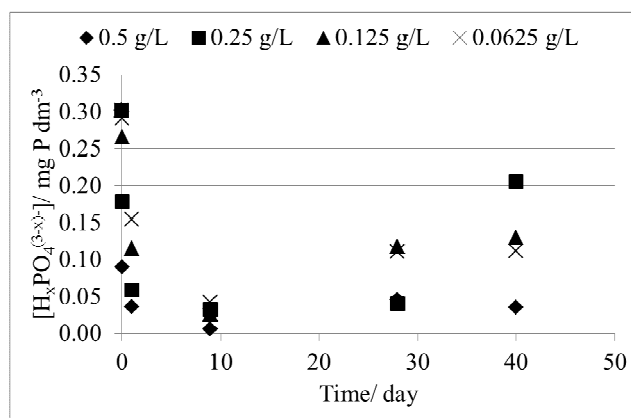

Figure 4: Long-term static contact of NCaSil and 0.3 mg P dm^{-3}.

NCaSil loading/ g dm^{-3}	Phosphate removal (40 d)	pH (40 d)
0.0625	63%	8.2
0.125	57%	8.2
0.25	31%	8.5
0.5	88%	8.8
1.0	90%	9.2
2.0	97%	10.5
4.0	> 99%	10.9

Table 1: Phosphate removal and final pH for NCaSil in long-term static contact with 0.3 mg P dm^{-3} solution.

3.4 Removal of Phosphate from Surface Water

The removal of phosphate from pre-filtered surface water by NCaSil is show in Figure 5. It can be seen that the adsorption of phosphate proceeds less rapidly than similar batch scale tests, for example those shown in Figure 1. The most likely cause for this is the speciation of phosphate present in the sample. The batch scale tests were conducted with the $H_2PO_4^-$ ion, and a corresponding initial pH of 5.4. The initial pH of the lake water sample was 9.0, meaning that any inorganic phosphate would be present primarily as the HPO_4^{2-} ion. It is known that mechanism of adsorption of phosphate by NCaSil procedes through an initial reaction of the NCaSil with acid, giving a positvely charged intermediate species. As such, the adsorption of HPO_4^{2-} occurs less rapidly than the adsorption of $H_2PO_4^-$ [8].

However, if long-term stability testing were to be conducted with this lake water, it is likely that phosphate release such as that seen in Figure 4 would be retarded as the higher pH of this lake water sample would retard the pH increase observed due diffusion of atmospheric carbon dioxide into the sample.
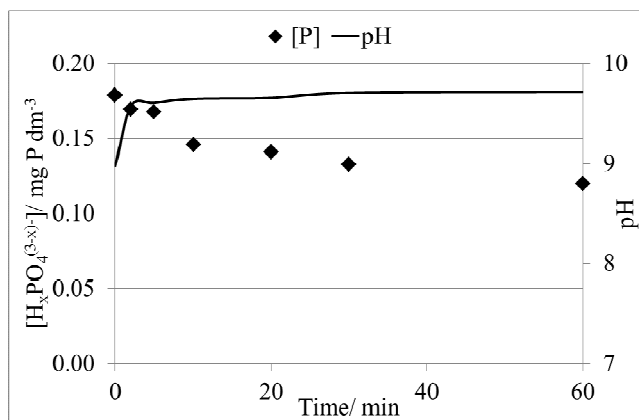
Figure 5: Uptake of phosphate by NCaSil from filtered lake water by NCaSil at a loading of 0.25 g dm^{-3}.

4 CONCLUSIONS

We have demonstrated the use of NCaSil as a material for the adsorption of phosphate from dilute solution. When batch adsorption tests were undertaken, the adsorption was rapid, proceeding to a total phosphate removal of > 87% within 10 minutes of contact time. Long-term static stability testing of the NCaSil revealed leaching of phosphate over time periods of several weeks. This was attributed to diffusion of atmospheric carbon dioxide into the test solutions, and a corresponding increase in solution pH.

Continuous uptake tests with either the unmodified NCaSil, or a magnetic composite material demonstrated that the material may be suitable for use in a system where the the phosphate is recovered for later re-use. However, for systems where the influent phosphate concentration is low (0.3 mg P dm^{-3}), correspondingly low adsorption capacities (0.5 mg P g^{-1} NCaSil), and significant release of calcium and silica into solution are also observed. When the initial phosphate concentration was increased to 31 mg P dm^{-1}, an adsorption capacity of 100 mg P g^{-1} Fe$_3$O$_4$-NCaSil was observed.

Testing of the NCaSil material as a phosphate adsorbent in a contaminated surface water provided low adsorption capacities and slow uptake rates, due to the high pH of the surface water sample. It is probable that use of NCaSil with surface water samples at a lower pH would show improved phosphate uptake.

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