THE REMOVAL OF PHOSPHATE BY HYDROXYAPATITE AND STRUVITE CRYSTALLISATION IN SOUTH AFRICA

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ABSTRACT

Nutrient removal by chemical means has, over the past decade, become an expensive practice owing to the scarcity of chemicals. A new method of phosphate removal by hydroxyapatite \([\text{Ca}_5(\text{PO}_4)_3\text{OH}]\) crystallisation has gained increasing interest as the need for the implementation of clean technology has become more apparent as we move into the environmentally conscious nineties. This method as well as another method, viz. struvite \([\text{NH}_4\text{MgP}0_4.6\text{H}_2\text{O}]\) crystallisation, will be discussed using results obtained from a laboratory scale study using three types of effluent, two demonstrating hydroxyapatite crystallisation and the third, struvite crystallisation. While it has been proven that phosphate crystallisation does work as a tertiary treatment (Van Dijk and Wilms, 1991) this paper will also show that the positioning of the crystalliser can vary to suit the need of the industry for which it has been designed.

KEYWORDS

Chemical phosphate removal, crystallisation, hydroxyapatite, struvite, fluidised bed.

INTRODUCTION

It is forecast that by the year 2030, all the presently available fresh water resources will be depleted in the PWV (Pretoria, Witwatersrand and Vereeniging) area. This study deals with effluent obtained from this area. Recycling of treated waste waters for suitable re-use will, amongst other possible solutions, be essential for commerce and industry. Consequently the protection of South Africa's natural and man-made fresh water supplies remains of paramount importance in the future, and thus the importance of effective phosphate removal should not be underestimated. Phosphate is generally regarded as a key nutrient in the eutrophication of rivers and lakes and its removal from wastewater to a level of 1 mgP/1 is laid down by law. The implementation of phosphate removal technologies in water treatment plants have classically consisted of chemical precipitations, biological processes, and combinations of biological processes with tertiary treatment. Immobilisation of the phosphate could be achieved in a combined process in which the known potential of organisms to concentrated phosphate could be used in tandem with a crystallisation reactor in which a side stream of the phosphate enriched water could be treated. Typical phosphate influent concentrations of 10 mgP/1 are easily increased to 60 mgP/1 as a consequence of release during the anaerobic phase. These increased
concentrations favour the formation of hydroxyapatite and make it feasible to treat a side stream instead of the full incoming stream. The phosphate granules which form in the crystallisation reactor can then be removed from the system and would have the advantage of occupying a very small volume relative to conventional secondary sludges. The technical feasibility of phosphate crystallisation as a unitary process has already been demonstrated by Zoltek (1974), Kokobori and Kyosai (1982), Joko (1984), and Van Dijk and Braakensiek (1984). These studies were, however, all carried out using either synthetic feed in batch tests or waste effluent after conventional treatment and separation by means of secondary settlement. It is therefore imperative that phosphate crystallisation in conjunction with the modern modified activated sludge process with their typical abilities of phosphate release, should be investigated. Crystallisation can be categorised into two processes, viz. nucleation and growth. Nucleation is the generation of crystals from solution. Growth is the process whereby ions are transported to the crystal surface and then orientated into the crystal lattice. Where there are only small concentrations of seed crystals such as in conventional precipitation processes, both nucleation and growth take place simultaneously, which is referred to as spontaneous or homogeneous crystallisation. When the crystal concentration is high such as in a pellet reactor, growth is the dominant process which is referred to as heterogeneous nucleation (Van Dijk and Wilms, 1991).

Crystallisation of hydroxyapatite \( (\text{HAP}) \), in aqueous solution is fundamental to this phosphorus removal method and is described in the equation:

\[
3\text{PO}_4^{3-} + 5\text{Ca}^{2+} + \text{OH}^- \rightarrow \text{Ca}_3(\text{PO}_4)_3\text{OH} \quad (1)
\]

The crystallisation of HAP should occur in the metastable supersaturated region of HAP. The crystallisation is commonly influenced by the nature of the seed crystal, phosphate concentration, calcium ion concentration, and the pH value of the effluent (Kaneko and Nakajima, 1988). The provision of a seed material onto which depositions of hydroxyapatite or struvite can occur is of vital importance to the successful operation of crystallisation systems. Work on hydroxyapatite crystallisation has been done using various seed materials, viz. phosphate rock, bone charcoal, magnesia clinker, zirconium hydroxide, pumice stone and sand. The magnesia clinker, bone charcoal and zirconium hydroxide were found to be the best and pumice stone the poorest. Phosphate rock and bone charcoal, however, are easily affected by bicarbonate alkalinity, which reduces phosphorus removal efficiency. Zirconium hydroxide has a weak crush strength and is therefore not a practical seed material. The special affinity these crystals have for phosphate is explained by a chemical reaction which occurs between the phosphate ions and the surface of the seed material (Kaneko and Nakajima, 1988). Joko (1984) obtained favourable results using phosphate rock, but these crystals were especially prepared for the experiment, thereby reducing its practical application.

There has not been much work done on struvite \( (\text{MAP}) \) crystallisation but it can, however, play an integral part in a sewage treatment plant. The chemical composition of digester supernatant liquor also favours the formation of the mineral, struvite, which can cause severe scaling and clogging on heat exchanger surfaces and in pipe networks. The introduction of waste activated sludge from nutrient removal plants, which typically contain up to five times as much phosphate and magnesium as 'traditional' activated sludge, compounds the struvite significantly. Pondering the fact that the RSA already has some 40 full-scale nutrient removal plants and that biological phosphate removal is gaining in popularity illustrates the growing need for technology which can effectively deal with the phosphate component of anaerobic digester supernatant. Struvite crystallisation could be used to immobilise part of the phosphate initially taken up by the waste microbial biomass and then released in the anaerobic digester. A stoichiometric amount of ammonia, which is another problem in sewage discharge, is immobilised as an additional advantage. The molecular ratio of struvite \( (\text{MAP}) \) is \( 1(\text{P}) : 1(\text{N}) : 1(\text{Mg}) \) calculated from the MAP formula. The kinetics of MAP are slow and complex. It would seem that relatively high supersaturation and moderately high pH levels are desirable for rapid crystallisation. Solutions of magnesium, phosphate and ammonia are easily supersaturated. The induction time for crystal formation is usually two days (Egan, 1989). Borgerding (1972) showed that solubility of MAP declines with rising pH, and the system should be kept at pH 8.00 or higher, to produce MAP.
Phosphate removal by hydroxyapatite and struvite crystallisation efficiently. The efficiency was dependant on the amount of magnesium added to the supernatant as well as increasing the pH of the supernatant with the addition of NaOH. Preliminary work was done on struvite crystallisation using yellow-shale and flyash as seed materials (De Waal et al. 1990). Although there was a substantial decrease in the phosphate, calcium and magnesium concentrations the ammonia remained constant. It must be noted, however, that yellow-shale and flyash are phosphorus, calcium and magnesium deficient, and will adsorb large quantities of these components until eventually becoming saturated. Magnesia clinker as a seed material was efficient in HAP crystallisation, although no work was done using this seed material in struvite crystallisation. As the phosphate crystallisation removal property of the magnesia clinker seems to be related to the accompanying release of a slight amount of magnesium ions (approx. 10mg Mg/l) into the solution (Kaneko and Nakajima, 1988), in doing so the magnesium concentration would be supplemented, thereby enhancing the chances of MAP formation. Preliminary work indicated that serpentine [Mg₃Si₂O₅(OH)₄] should function readily as an excellent adsorbent for phosphate. It is available in large quantities in some parts of the U.S.A and could easily be mined using open-cast techniques. When serpentine is added to water there is a considerable pH increase and magnesium ions are released into the water. An increase in pH releasing magnesium ions would thereby precipitate some phosphate. Therefore this has potential for removing ammonia-nitrogen because of the pH rise and the possibility of MAP formation as well as the possible adsorption of ammonium ions on silica sites on the serpentine. The best known serpentine form is chrysotile (Smith and Hwang, 1978). Although serpentine has been used for phosphate adsorption rather than crystallisation it may well have potential as a seed material for MAP crystallisation.

The effective and efficient removal of phosphate by hydroxyapatite crystallisation, using a sewage works final pond effluent and an abattoir effluent, and struvite crystallisation using an anaerobic digester supernatant will be demonstrated. The choice of these effluents is deliberate as they vary in complexity, and by showing that the crystallisation process can remove phosphate from these effluents, the versatility of the system can be demonstrated. Quartz sand was concentrated upon as a seed material since it was the most readily available and easily accessible.

MATERIALS AND METHODS

A laboratory-scale system which comprised six reactors was used in all experiments (Fig. 1). The reactors were made from perspex and 50mm in diameter and 11250mm in length.

![Diagram of laboratory-scale reactors](https://iwaponline.com/wst/article-pdf/26/5-6/987/113511/987.pdf)

**Fig. 1.** A frontal view of one of the six laboratory scale reactors
The effluent was fed at a controlled rate by means of a diaphragm valve and a rotameter into a perspex 'bucket' into which a Schott Geräte (N9020) electrode was placed to monitor the pH and the set pH level was maintained by the addition of either 0.1N or 1N NaOH depending on the alkalinity of the effluent (Fig. 2). The NaOH addition was controlled by a Programmable Logic Controller linked to solenoid valves.

![Fig. 2. The pH control 'bucket' (right) and the rotameter (left)](image)

An amount of 500g of acid (HCl) washed quartz sand was placed into each reactor and the particle size of the sand is presented in Table 1. The sand under operating conditions was fluidised to twice its resting volume by pumping the pH adjusted effluent from the 'bucket' into the bottom of the reactor (Fig. 3). The retention time was calculated on the basis of the height of the sand in the fluidised bed and the feed rate of the effluent.

![Fig. 3. A schematic diagram of laboratory-scale system](image)
Phosphate removal by hydroxyapatite and struvite crystallisation

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TABLE 1 The particle distribution of the sand used in the reactors of the laboratory-scale system

Three effluents were used in the experiments; these were collected from a sewage works final pond effluent, an abattoir activated sludge biological clarifier effluent, and an anaerobic digester supernatant. All effluents were collected respectively and stored in a holding tank. While the final pond effluent and the abattoir effluents were used without further preparation, the anaerobic digester supernatant had to be centrifuged (Alfa Laval sewage centrifuge). This was due to the presence of excessive particulate matter in the effluent which would block the rotameters on the laboratory scale system. This, however, would not pose a problem in a pilot or full scale plant. Initial experimentation was carried out on the final pond effluent at a pH range of 8.0 to 9.5 using a retention time of ten minutes. The experimentation then continued adjusting the above parameters as well as the calcium, phosphate and magnesium concentrations in an attempt to optimise the condition of the effluent for the most efficient and effective hydroxyapatite or struvite crystallisation respectively depending on the nature of the effluent.

Sampling was conducted hourly from the top ports of the reactors, except for one experiment where the samples were taken every minute in an attempt to determine the rate at which the reaction constituting the phosphate removal took place. The samples were filtered through Whatman no. 1 filter paper and stored overnight in a fridge. All samples were analysed according to Standard Methods (Clesceri et al. 1989) on a Technikon Auto Analyser and a Varian 1275 Atomic Absorption Spectrophotometer, respectively. During all experiments the temperature in the reactor ranged between 25°C, when the first sample was taken, and 40°C, when the last sample was taken.

RESULTS AND DISCUSSION

To establish a basis of how effective the system was, hydroxyapatite crystallisation was concentrated upon. An initial experiment was conducted using the final pond effluent with the pH range of 8.0 to 9.5 at a ten minute retention time. Although there was some phosphate removal, indicating that the system was functioning, it was not very substantial, with a removal in the order of 5 mgP/l at pH 9.5 (Fig. 4). It was then that the systematic evaluation of the system began, by adjusting each parameter and assessing the effect on the phosphate removal, and thereby optimising the system. The pH range was adjusted to a range of 8.6 to 10.6. The phosphate removal improved but it was considered that the removal could be further improved as a low calcium concentration could be limiting. It was observed at this time that there was little difference between a 10 and a 3 min retention time, as there was an 89% and a 90% phosphate removal at both retention times respectively. It can be deduced from the HAP molecular formula that the Ca:P ratio must be in the order of 2:1 for efficient HAP formation. Supplementation of the effluent with calcium (CaCl2) resulted in a substantial improvement in the removal, viz. from the order of 9 mgP/l to 0.1 mgP/l at pH 10.6 (Fig. 5).

During the hour from when the experiment commenced and the first sample was taken, the total removal possible at those parameters had occurred and remained constant throughout the experiment. It was thus considered that the rate of the reaction constituting the phosphate removal would have
an important bearing on the economic aspect of the system. The results showed a removal from 10mgP/l to below 1mgP/l in 1 min. and remained constant at below 1mgP/l for the duration of the experiment, this time could be less as the sampling was done every minute.

![Graph](image1)

**Fig. 4.** Phosphate removal at pH range 8.0 to 9.5 using unsupplemented final pond effluent and a 10 min retention time

![Graph](image2)

**Fig. 5.** Phosphate removal at pH range 8.6 to 10.6 using calcium supplemented final pond effluent

As one of our aims was to test the versatility of the system a more complex effluent was used, viz. an abattoir effluent. The most apparent differences between this effluent and the final pond effluent was the increased phosphate and alkalinity concentrations. It was discovered that due to the higher alkalinity, the effluent required a larger volume of NaOH to maintain the required pH level. As this would have a direct bearing on the economics of running a crystalliser a table (Table 2) was compiled illustrating the conversion of NaOH to lime [Ca(OH)$_2$] giving a calculated mass of how much lime would be needed to adjust the pH of each effluent used in this study to the required level. NaOH was used in the laboratory scale system for practical purposes, but when scaling up to pilot or full scale plants it would be more economical to use lime. The function of lime would then be two-fold as it would maintain the pH level as well as supplementing the calcium concentration thereby enhancing the HAP formation. Although there was a substantial decrease in the phosphate concentration, from 40mgP/l to 10 mgP/l, the calcium concentration again proved to be insufficient for removal to below 1mgP/l. On supplementing the effluent with calcium, the most efficient removal was at pH 10.6 where the phosphate concentration was decreased to 0.1mgP/l (Fig. 6). At pH 9.8 the phosphate was removed to 1mgP/l and at pH 9.0 to 10mgP/l. This is especially important for industries where the water regulation is more lenient and the discharged waste water must be <10mgP/l.
To establish the basic parameters for MAP formation, as in the hydroxyapatite crystallisation, the initial experiment was conducted using unsupplemented effluent operating within a narrow pH range of 8.9 to 9.8. On the basis of these results it was thought to optimise conditions for effective and efficient struvite crystallisation. Fig. 7 depicts no substantial removal of phosphate, averaging 5mgP/l, at the various pH levels, suggesting a limiting factor. There was, however, a substantial calcium utilisation, 140mg Ca/l, indicating HAP formation or softening (CaCO₃), rather than MAP formation.
The Mg : N : P ratio for effective MAP formation is calculated according to molecular weight:

\[
\frac{Mg}{N} : \frac{N}{P} : \frac{P}{N} = 24 : 14 : 31 = 69
\]

Simplified:

\[
\frac{Mg}{N} : \frac{N}{P} : \frac{P}{N} = 1.71 : 1 : 2.21 \text{ therefore if } N = 69 \text{ then }
\]

\[
116 : 69 : 150 \text{ mg/l}
\]

The magnesium and phosphate were supplemented to the concentrations stipulated in the last ratio demonstrated above to produce the recipe for the most effective and efficient MAP formation. The pH range was also increased and thus ranged from 7.0 to 9.5. It was interesting to note that the supplemented components were not reflected when the effluent was analysed before commencing the experiment. It was only after the addition of concentrated HCl that the supplementations were evident but the alkalinity was almost totally removed. The phosphate removal was substantial, from 198mgP/l to 5mgP/l (Fig. 8), as was the calcium utilisation, 201mg Ca/l to 13mg Ca/l, the magnesium utilisation, 121mg Mg/l, and more than half of the ammonia was utilised, from 296mg NH₃/l to 173mg NH₃/l. All these values were at a pH of 9.5, and it was apparent that there was definite MAP formation, which was better at the higher pH levels while removal and utilisation at the lower levels was negligible.
To establish the effect of more acidic and alkaline pH levels on MAP formation, the pH range from 6.5 to 11.5 was investigated. As illustrated in Fig. 9, no real difference was observed at the higher pH levels.

Fig. 9. The phosphate removal at pH range 6.5 - 11.5 using supplemented anaerobic digestor supernatant

**CONCLUSION**

The technology for both HAP and MAP crystallisation is fundamentally the same with only slight differences occurring in the parameters. Both processes are reliant on the nature of the seed material, the phosphate concentration and the pH level, viz. an alkaline effluent not lower than pH 9.5 for hydroxyapatite crystallisation and not lower than pH 8.0 for struvite crystallisation.

The only major difference is the reliance on the calcium ion concentration for HAP crystallisation and the magnesium and ammonia concentrations for struvite crystallisation. Sand proved to be a suitable seed material for both processes and is inert enough not to cause concern when the crystals are removed from the reactor to be spread out on agricultural land as fertiliser (HAP crystals), and a slow release fertiliser (MAP crystals).

It is apparent for removal to be efficient and effective by either process, the ratios pertaining to the phosphate, calcium, magnesium and ammonia concentrations respectively must be adhered to as closely as possible.

While a considerable amount of work has been done on phosphate removal by hydroxyapatite crystallisation on an international basis and the studies have concentrated on the removal taking place as a tertiary treatment, this a relatively new technology in South Africa and this study has concentrated on demonstrating that not only is this process versatile but there is another form of phosphate removal available, viz. struvite crystallisation, which can be of value in the prevention of scaling clogging in sewage pipeline networks. Fig.10 shows the versatility of both processes in that they can be instituted at various points in a sewage system. It must also be noted that the crystallisation systems can be adapted to suit other industries as well, in that the design of the reactor can be structured around the requirements of a particular industry.
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REFERENCES