



## Struvite production using membrane-bioreactor wastewater effluent and seawater



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### ABSTRACT

Wastewater phosphorus (P) released into natural water bodies such as lakes and rivers, can cause water pollution as a result of eutrophication. If this P is effectively removed from wastewaters and economically recovered for use as fertilisers, not only can the water pollution be controlled, but also reduce the anticipated global shortage of P. This scarcity will result from the natural phosphate rock reserve being exhausted. Three experiments were conducted using membrane-bioreactor effluent (MBR, 35 mg PO<sub>4</sub>/L) and reverse osmosis concentrate (ROC, 10 mg PO<sub>4</sub>/L) waters to supply phosphate, and sea water (1530 mg Mg/L) to supply Mg for the production of struvite. The phosphate in the MBR and ROC was concentrated approximately 15 times by adsorption onto an ion exchange resin column followed by desorption. Struvite was precipitated by mixing the desorbed solution with seawater and NH<sub>4</sub>Cl. The chemical composition and mineral structure of the precipitates agreed with those of the reference struvite. When Ca in seawater (300 mg Ca/L) was removed before mixing the water with MBR or ROC, the purity of the struvite improved.

### 1. Introduction

Wastewater with high concentration of phosphorus (P) entering natural water bodies commonly causes eutrophication. Therefore, P should be removed from these wastewaters before discharge. The recovery of the removed P in the form of P fertilisers can reduce the anticipated future shortage of high-quality phosphate rocks used to make P fertilisers [1–4].

A simple, efficient and cost-effective method of removing phosphate from wastewaters is to adsorb the phosphate onto an adsorbent that has a high adsorption capacity of P and then subsequently extracting the adsorbed phosphate by eluting with a suitable reagent. The phosphate that is recovered may be precipitated with Ca or Mg/NH<sub>4</sub> salts and employed as P fertilisers. Precipitation with Ca produces hydroxyapatite fertiliser while that with Mg and NH<sub>4</sub> salts produces struvite fertiliser. Hydroxyapatite fertiliser has been generally produced by adsorption of wastewater phosphate onto ion exchange resins coated with Fe and desorbing the adsorbed phosphate using NaOH/NaCl [5–7]. Spontaneous struvite crystallisation and its negative impact on wastewater treatment plants' operations such as clogging of pipelines and pumps have been well documented [8]. The principles of this struvite crystallisation process have been extended to producing struvite of high purity under controlled conditions [9–12]. Of the two types

of fertilisers that can be produced from wastewaters, struvite is preferred, provided that the production costs can be controlled, especially ensuring that the raw materials are not expensive. Also, struvite contains two additional nutrients, Mg and NH<sub>4</sub>.

Most research conducted in the production of struvite has employed synthetic solutions. Many studies have used real wastewaters of different types but added Mg salts such as chlorides, sulphates, oxides and hydroxides [11, 12]. Some have successfully used bittern (a salt industry by-product) as a source of Mg with wastewater from swine farms for the production of struvite [13, 14]. Since seawater has a high concentration of low-cost Mg (1290 mg/L, [15]), seawater nanofiltration concentrate [16] or seawater reverse osmosis concentrate [17] have also been mixed with wastewaters to produce struvite.

Wastewaters used in the above studies may contain various types of heavy metals which could get incorporated into the struvite that is produced and when used as a fertiliser can cause environmental problems. This problem may be overcome if the wastewaters are initially pre-treated to remove unwanted metals. The membrane bioreactor (MBR) is an attractive process in wastewater treatment because it can remove solids, nutrients and dissolved organic carbon, with minimum sludge production and possess a high loading rate capacity [18]. It can also effectively remove most of the heavy metals partly due to the heavy metals' capacity to be retained on the suspended solids generated

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in the biological process in the MBR [19]. However, it cannot completely remove phosphate [18]. This would make MBR effluent a good source of phosphate for struvite production as it contains minimum concentrations of heavy metals that could contaminate struvite.

The objective of this study was to produce struvite using MBR effluent and reverse osmosis concentrate (ROC) from urban domestic wastewater reclamation plants as the phosphate source and seawater as the Mg source. The phosphate in the effluent and ROC was concentrated by adsorption on an ion exchange resin followed by recovery of the adsorbed phosphate by desorption and used in struvite precipitation. This technology is useful, cost-effective and can be implemented at locations near the sea. To the best of our knowledge, no study of this nature has previously been reported.

## 2. Materials and methods

### 2.1. Materials

MBR water from a waste water reclamation plant, Sydney, Australia and ROC of a secondary wastewater treated water from another waste water reclamation plant, were used as the phosphate source for the production of struvite. This MBR water contained  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  concentrations of 26, 35 and 33 mg/L, respectively, and the ROC water had  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  concentrations of 46, 10 and 74 mg/L, respectively. The pH of the MBR water was 7.0–7.5 and that of ROC was 7.5–7.8. The Seawater collected from Chowder Bay, Sydney with Na, Ca, Mg, and K concentrations (g/L) of 12.82, 0.30, 1.53, and 0.49, respectively and pH 8.3–8.7, was used as the Mg source. Analar grade  $\text{NH}_4\text{Cl}$  obtained from Sigma-Aldrich, USA was used to precipitate the struvite. Though the  $\text{NH}_4$  used in the production of struvite is a commercial source in the form of a nitrogen fertiliser, the added  $\text{NH}_4$  remains in the final struvite product which can therefore serve both as a phosphate and a nitrogen fertiliser. A strong base Styrene-DVB matrix anion exchange resin, Dowex 21K XLT, was used in the study. The properties of this resin were presented elsewhere [7].

### 2.2. Struvite precipitation method

Three struvite precipitation experiments were conducted in glass flasks containing MBR and ROC waters. These solutions supplied the phosphate component of the struvite. Seawater was added to these waters to provide the Mg component of the struvite, and Analar grade  $\text{NH}_4\text{Cl}$  was added to the solutions to provide the struvite's  $\text{NH}_4$  component. The Mg and  $\text{NH}_4$  ions react with  $\text{PO}_4$  to form struvite precipitate. The  $\text{NO}_3$  and  $\text{SO}_4$  in the MBR and ROC would not compete with  $\text{PO}_4$  in the precipitation of struvite because  $\text{MgSO}_4$  and  $\text{Mg}(\text{NO}_3)_2$  are highly soluble ( $\text{MgSO}_4$  solubility product  $K_{sp}$  4.67) compared to  $\text{MgPO}_4$  ( $K_{sp}$   $1 \times 10^{-24}$ ) or struvite ( $K_{sp}$   $3 \times 10^{-13}$ ). The details of the experiments and the pre-treatment applied to the solutions such as removal of Ca from the solutions, are presented under separate experiments in the next section. The mixed solutions were agitated in a flat shaker at a speed of 150 rpm for 3 h at room temperature ( $24 \pm 1$  °C). The precipitates that were produced were separated by filtration and washed with demineralised water to remove any soluble ions present. They were kept in an oven to dry at a temperature of 40 °C for 24 h. After this, their weights were measured.

#### 2.2.1. Struvite 1: struvite precipitation using seawater and MBR water (without Ca removal)

The MBR water was utilised as the phosphate source in this experiment. To obtain the phosphate required for struvite precipitation, firstly the phosphate in the MBR solution was adsorbed onto 56 g of the ion exchange resin packed inside a glass column. To provide a uniform flow of the MBR water to the column the base of the column was filled with a layer of glass beads and held in place by a stainless-steel sieve attached to the bottom of the column. MBR water was pumped upward

through the column at a filtration velocity of 2.5 m/h. The breakthrough curve obtained for phosphate adsorption on Dowex 21K XLT reached saturation after 47 h and approximately 68% of the adsorbed phosphate was desorbed by 0.1 M NaCl within the first 30 min (42 bed volumes). The phosphate concentration in the 600 mL desorbed solution collected during this period was 0.0052 M. This concentration is 14 times higher than that in the original MBR water. Struvite 1 was made by mixing 200 mL of the above desorbed solution with seawater and  $\text{NH}_4\text{Cl}$  at a phosphate,  $\text{NH}_4$  and Mg molar ratio of 1:1:1. This ratio was reported to be the optimum condition for the precipitation of struvite [7, 11].

#### 2.2.2. Struvite 2: struvite precipitation using seawater and MBR water (with Ca removal)

In this experiment, struvite was precipitated using 200 mL of the desorbed solution obtained in the Struvite 1 experiment, except Ca was removed as  $\text{CaCO}_3$  from the seawater. This was done by adding  $\text{Na}_2\text{CO}_3$  at a Na to Ca molar ratio of 2:1, before mixing this solution with the desorbed solution. Ca was removed because it may interfere with the precipitation of struvite [12].

#### 2.2.3. Struvite 3: struvite precipitation using seawater and ROC water (with Ca removal)

In this experiment, struvite was precipitated using seawater as the Mg source as in Struvite 1 and 2 precipitations; further more ROC water instead of MBR water was used. Ammonium was added to this water in the form of  $\text{NH}_4\text{Cl}$ . Because the phosphate concentration in this ROC was low, the ROC was spiked with phosphate by adding  $\text{KH}_2\text{PO}_4$  to increase the concentration to that in the MBR used in the earlier experiments (35 mg/L). The ROC had 95% of the total phosphorus in the form of orthophosphate. The phosphate in the spiked solution was further concentrated by adsorption/desorption as described in the Struvite 1 experiment. The high salinity of ROC is not expected to interfere with struvite precipitation because the anion exchange resin has very low affinity to adsorb the monovalent Cl anion in the presence of strongly adsorbing phosphate, sulphate and carbonate and Na which is a cation cannot adsorb to the positively charged anion exchange resin. Also Na does not react with phosphate to form precipitate. The breakthrough curve for phosphate in the ion exchange column reached saturation after 42 h and approximately 72% of the adsorbed phosphate was desorbed by 0.1 M NaCl within the first 30 min (42-bed volumes). The phosphate concentration in the desorbed solution was 0.0059 M. Calcium was removed from the seawater as described before and the resulting solution was mixed with  $\text{NH}_4\text{Cl}$  and the desorbed solution to produce Struvite 3.

### 2.3. Chemical analysis

The chemical analysis of the struvites that were produced was conducted by dissolving 0.1–0.2 g of dried precipitate in 100 mL of 1% (w/w)  $\text{HNO}_3$  solution. The suspensions were filtered and the concentrations of phosphate,  $\text{NH}_4$ , Mg, Ca, Na, K in the filtrate were measured. Phosphate was analysed using a model 790 Personal IC ion chromatograph (Herisau, Switzerland). The metals' (i.e. K, Na, Ca, Mg) concentrations were measured using Microwave Plasma - Atomic Emission Spectroscopy (MP-AES) (Agilent 4100). Ammonium was analysed employing the cell test method (Spectroquant, Merck, Darmstadt, Hesse, Germany) with a photometer (NOVA 60, Merck). The pH was measured using a HQ40d portable pH Meter (Hach, Loveland, CO, USA).

### 2.4. Characterisation of mineral structure

The structure of the struvite was determined using X-ray diffraction (XRD). XRD was carried out using a PANalytical Empyrean instrument operated at 60-kV with Cu-K $\alpha$  radiation on powdered samples of

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