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Use of concentrate water from seawater desalination plant as magnesium sources for struvite formation by using anaerobically digested effluent of swine wastewater

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ABSTRACT

Although struvite crystallization has been proven an effective process to recover nutrients from wastewater, this method has not been used widely because of the cost of the raw chemicals, such as magnesium chloride, required as supplements. In this study, in view of the high cost of supplementing magnesium, reject water from a seawater reverse osmosis process was investigated as a potential source of magnesium. The magnesium was used in the nutrient recovery process, by which struvite crystallization was performed from the anaerobically digested effluent of swine wastewater. The results of all the experiments were positive, indicating that struvite formation was successfully performed from the effluent, using the concentrate water as a magnesium source. Removal efficiencies of up to 94.5% for phosphate and 12.7% for ammonium were achieved under normal operating conditions. Seed materials were successfully used as nucleation sites to enhance the purity of the struvite and the crystal size. The removal efficiencies of phosphate and ammonia could be improved up to 97 and 84%, respectively, by adding phosphate and seed materials.

Keywords: Concentrate water; Magnesium ammonium phosphate; Phosphorus recovery; Seawater desalination; Swine wastewater; Struvite

1. Introduction

Recently, animal wastewater treatment and recycling have been instituted in South Korea, given that the volume of animal wastewater generated in the country is estimated at approximately 46,000 Mm^3/yr. Anaerobic digestion has often been adopted as a treatment for animal waste because of the efficient conversion of high-strength organics and the production of beneficial biogas [1,2]. However, anaerobic digestion discharges effluent high in nutrients that can cause eutrophication in water bodies. In Korea, the effluent from anaerobic digesters is required to undergo

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advance treatment to meet the stringent discharge criteria of 0.2 mg/L phosphate as phosphorus [3].

However, pig farming leads to considerable social and economic problems because of the negative effect on the environment associated with the treatment and recycling of swine wastewater [4,5]. Nevertheless, one of the best ways to recycle wastewater nutrients is for agricultural use. The nutrients recovered from the anaerobically digested effluent of swine wastewater can be a potential source of fertilizer, partially offsetting the wastewater treatment costs. Particularly, the depletion of phosphorus resources has been a major concern and a topic of discussion worldwide [6], although it is estimated that 7,000 million ton of phosphate rock exists. Crystallization processes, such as struvite and hydroxyapatite, are preferred to achieve these objectives [3,5]. Struvite ($MgNH_4PO_4{\cdot}6H_2O$) has a potential use in agriculture as fertilizers. Struvite crystallization has been proven an effective process to recover nutrients from wastewater for numerous reasons [7,8].

Magnesium plays an important role in the struvite crystallization process to recover phosphorus from wastewater, as it consumes the magnesium ion [9,10]. Struvite is a crystalline substance consisting of magnesium, ammonium, and phosphorus in equal molar concentrations; therefore, an additional magnesium source is usually required to produce struvite crystals [11]. The concentration of magnesium in the effluent of anaerobic digesters is usually lower than those of ammonium and phosphate, and extra magnesium has to be added to ensure struvite crystallization. Although, a number of factors, such as pH, reactor configuration, and the molar ratio of components, struvite crystallization process is not widely used because of the additional cost of adding magnesium supplements, such as magnesium chloride, magnetite, and magnesium sulfate. However, adding synthetic chemicals is relatively expensive [12,13], which negatively influences the economic feasibility of the process. Consequently, it is important to find an alternative, cheaper source of magnesium.

The magnesium ion is a common component in the sea (approximately 1,300 mg/L); therefore, seawater could be an economically viable source of magnesium [14]. Although salinity increases with distance from land, the magnesium concentration of the seawater at the coast is adequate for this water to be used in wastewater treatment. Therefore, wastewater treatment plants close to the coast could use the magnesium directly from the seawater for struvite crystallization [15,16]. In comparison with using $MgCl_2$ chemicals, a significant reduction in operating costs was achieved when seawater was used as a magnesium source in a struvite pilot plant to treat the effluent from an anaerobic digester [17]. Although seawater could be a suitable source of magnesium for the struvite crystallization process, the cost of pumping or haulage of this water has to be considered. A nanofiltration-based method was investigated for selective separation of magnesium ions from seawater, with the aim of using the magnesium-loaded brine for either enrichment of magnesium ions or for enhancement of struvite crystallization from wastewater steams [18].

In 2013, there were more than 17,000 seawater desalination plants worldwide that produced freshwater and brackish water [19]. The desalination process concentrates the dissolved salts and other materials from the seawater and brackish water during the purification of the water. Seawater is passed through a reverse osmosis or nanofiltration membrane in desalination plants, which separates the ions. Consequently, the nanofiltration brine is rich in ions, including the magnesium ion. The reject water from the desalination plant is a considerably richer and more sustainable source of magnesium than seawater, as the reject water could be a free source of magnesium that would otherwise be discharged into the ocean [20,21]. The magnesium-rich concentrate, the reject from seawater desalination, has been used to promote struvite precipitation from wastewater [22].

In this study, in view of the high cost of supplementing magnesium, the concentrate water from a seawater desalination plant was investigated as a potential source of magnesium. The magnesium was intended for use in the nutrient recovery process by means of struvite crystallization from anaerobically digested effluent of swine wastewater.

2. Materials and methods

2.1. Concentrate water

A suitable treatment method is required for the concentrate water from seawater desalination because of the high salinity of this water. However, reverse osmosis is often chosen for desalination plants because of the proven ability of this method to produce high-quality water in an efficient way. In this study, concentrate water intended for use as a magnesium source was prepared from a reverse osmosis seawater desalination pilot plant in Gwangyang city, Korea. For comparison, $MgCl_2{\cdot}6H_2O$ was used as reagent chemicals in the struvite crystallization process. The initial concentrations in the seawater concentrate were 2,360 mg/L magnesium, 33,513 mg/L chloride, 17,616 mg/L sodium, 738 mg/L calcium, 682 mg/L potassium, and 33,092 mg/L TDS, as shown in Table 1.

Table 1
Composition of seawater concentrate

	TDS (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Chloride (mg/L)	Bicarbonate (mg/L)	Sulfate (mg/L)
Seawater	33,092	400	1,260	10,056	403	18,318	129	2,526
RO Reject water	59,708	738	2,364	17,616	682	33,513	205	4,590

2.2. Anaerobically digested effluent of swine wastewater

The anaerobically digested effluent of swine wastewater used in this study was obtained from P-city in Korea. For struvite crystallization, the wastewater sample was collected and concentrated by setting at 4℃ for 24 h. The main characteristics of the concentrated sample are shown in Table 2. The average concentrations of ammonia nitrogen and phosphate phosphorus were 1,775 and 221 mg/L, respectively. Whereas the ratio of the phosphate phosphorus to the total phosphate was only 40%, the ratio of the ammonia nitrogen to the total nitrogen of the digested effluent was more than 76%. The molar ratio of ammonia nitrogen to phosphate phosphorus was 18; consequently, a post-treatment process, such as ammonia stripping or phosphate addition, was needed to ensure ammonia recovery. For that reason, the molar ratios of ammonium, magnesium, and phosphate had to be considered in this experiment.

2.3. Reactor operation

The struvite crystallizations were synthesized by means of the molar ratio of the magnesium and phosphate as $Mg^{2+}:PO_4^{3-} = 1.2:1$, according to the indications of previous research [7,16,23]. Phosphate (KH_2PO_4) was injected as $NH_4^+:PO_4^{3-} = 1:1$ to improve the removal of ammonia nitrogen. The initial pH of the digester effluent sample was adjusted to 9.0 at the start of the experiment, using 0.1 NaOH solution. Furthermore, the natural zeolite used as seed, injected to improve the struvite crystallization, (the same conditions) that the struvite seed material was prepared as 75–150 μm by sieves. The characteristics of the zeolite seed used in this study are shown in Table 3. The schematic diagram of the experimental apparatus for struvite crystallization is shown in Fig. 1. The reactor operated with 10 min hydraulic retention time for mixing zone and 3 h for whole reactor. Then, the obtained struvite cake was dried at room temperature to form a powder.

Table 2
Characteristics of effluent from anaerobically digested swine wastewater

	Concentration
pH	8.17
T-N (mg/L)	2,350
NH_3-N (mg/L)	1,775
T-P (mg/L)	612
PO_4-P (mg/L)	221

2.4. Analysis

The feed and the treated samples in this study were filtered with 0.45-μm syringe filters to remove the suspended materials before analysis. The ammonia nitrogen was measured by using a HACH DR-5000 according to the Salicylate Method, as indicated in the HACH DR-4000 manual (DR5000, HACH Inc., USA). The phosphorous concentrations were determined by the ascorbic acid method, using a UV–vis spectrophotometer at 800 nm (Smart Plus SP-1900PC, Woongki Science, Seoul, Korea). The particle size distribution was measured by a particle size analyzer (Malvern Mastersizer S, UK). The pH meter (Orionstar, ThermoScientific, USA) was calibrated after each experiment. After struvite crystallization, the precipitates were dried at room temperature, and the type and shape of the crystals were identified with XRD (X-ray diffraction) analysis, employing the X-ray diffractometer (Advance D8, Bruker Co., Germany) and a microscope (Olympus BX51, Japan).

3. Results and discussion

3.1. Formation of struvite by using concentrated seawater

The results of all our experiments showed that struvite formation was successfully performed from the anaerobically digested effluent of the swine wastewater, using the concentrate water of the seawater reverse osmosis process as a magnesium source.

Table 3
Characteristics of zeolite seed

	Al	C	Ca	Fe	K	Mg	N	Na	O	Si
%	3.97	10.42	0.61	0.88	1.08	1.21	1.07	3.22	55.75	21.79

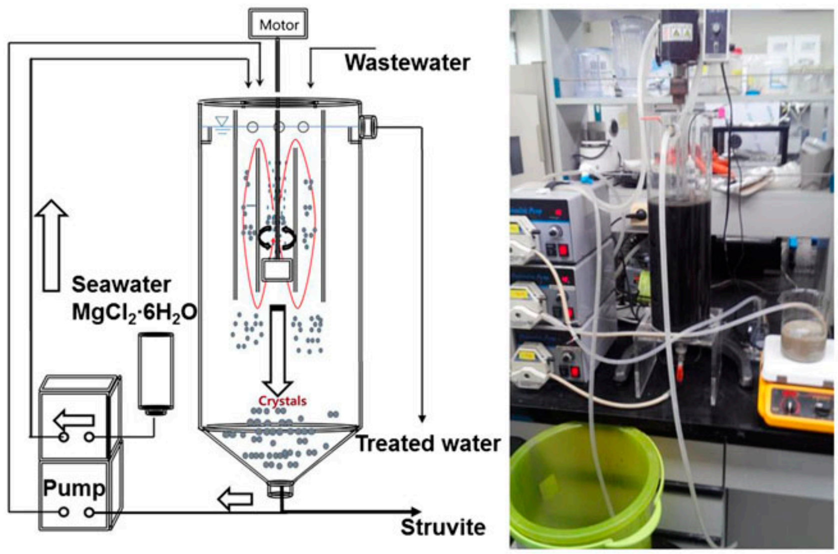

Fig. 1. Experimental equipment for struvite crystallization.

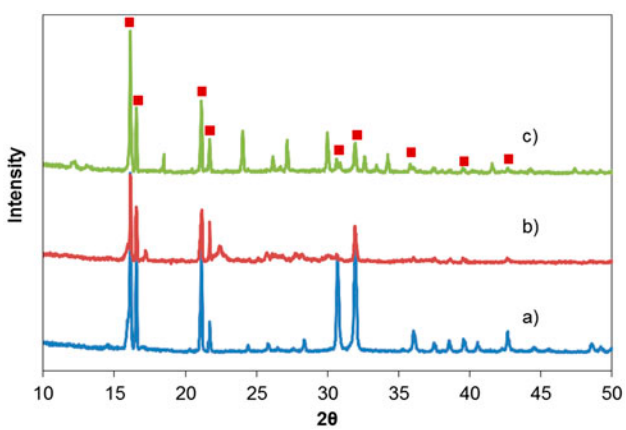

Fig. 2. XRD analysis of the collected struvite precipitates: (a) MAP ($MgCl_2$), (b) MAP (swine wastewater), (c) MAP (swine wastewater with seed).

The struvite crystals were analyzed by XRD to identify the powder as struvite. The parameters of the crystals formed from the seawater and the seed nuclei, shown in Fig. 2, corresponded to that of the synthetic struvite made of $MgCl_2$. The XRD pattern of struvite made of swine wastewater matched very well with that of the synthetic struvite. The noise peaks in MAP (wine wastewater) might be due to the amount of impurity present in the struvite crystals. A comparison with the standard XRD pattern database also indicated that the precipitates obtained were struvite crystals.

3.2. *Effect of phosphate injection*

Removal efficiencies of up to 94.0% for phosphate and 13.2% for ammonium were achieved under normal operating conditions, with the $MgCl_2$ as magnesium source. When the concentrated seawater was used, the removal efficiencies for phosphate and ammonia were 94.5 and 12.7%, respectively. These results indicate that the concentrated seawater can be used for struvite formation from the ammonium and phosphorus in the digester effluent. The molar ratio of ammonium and phosphate was 18:1 in the sample from the digester effluent; consequently, phosphate (KH_2PO_4) was added to increase the removal efficiency for ammonia nitrogen. The removal efficiency for ammonia with $MgCl_2$ and with the concentrated seawater increased to 93 and 84.2%, respectively (Table 4).

Table 4
Removal efficiency of ammonia and phosphate

	$MgCl_2$		Concentrated seawater	
	NH_3-N removal (%)	PO_4-P removal (%)	NH_3-N removal (%)	PO_4-P removal (%)
w/o P addition	13.2	94.0	12.7	94.5
w/P addition	93.1	96.4	84.2	97.3

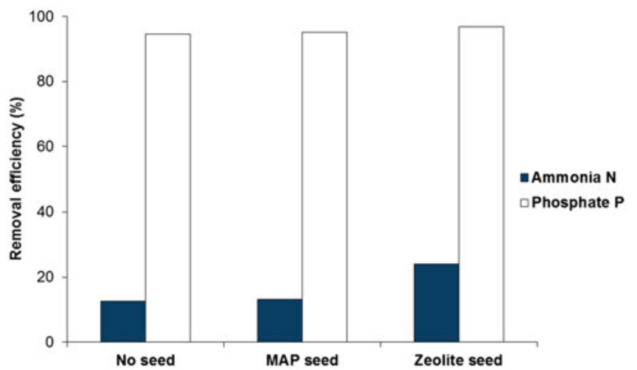

Fig. 3. Ammonia and phosphorus removal efficiencies.

3.3. *Effect of seed materials*

The crystallization of struvite occurs in two chemical phases, namely, nucleation or crystal birth and crystal growth [24]. Seed crystals can significantly reduce the induction and equilibration times, especially for solutions with a lower supersaturation ratio [25]. In the present work, recycling the synthesized struvite to the reactor and injecting zeolite as an external material were applied to act as a seed substrate for struvite crystallization in the digester effluent and the concentrated seawater. Fig. 3 shows the effects of the seed materials on the removal efficiencies for ammonia and phosphorus. The removal efficiencies for phosphate with no seed, MAP seed, and zeolite seed were 94.5, 95.2, and 96.9%, respectively. At the same time, the removal efficiencies for ammonia with no seed, MAP seed, and zeolite seed were 12.7, 13.1, and 24.0%, respectively. The effect of the seed materials on the removal efficiency for ammonia was much higher than on the removal efficiency for phosphate. The removal of ammonia nitrogen was significantly increased when zeolite was used as seed and it was assumed that the ammonium ions could be adsorbed on to the zeolite.

Fig. 4 shows images obtained from an optical microscope, indicating the struvite crystal synthesized effect on the seed materials. Crystal formation occurs by deposition of the precipitate constituent ions on to the seed. The result shows an increase in the size of the struvite crystal. Moreover, adding the seed increased the effect on the struvite synthetic materials and obtained results that were superior to those of the no seed condition.

Particle size has an effect on the dissolution rate and as the larger struvite granule releases the nutrients more slowly, it is superior as fertilizer [24]. Fig. 5 shows examples of the volumetric distribution of the crystal sizes of the product, obtained from the struvite crystallizer at pH 9. Clearly, the particle size was increased by adding the seed materials. Furthermore, the natural zeolite appeared to be the more effective seed compared with the synthesized struvite seed.

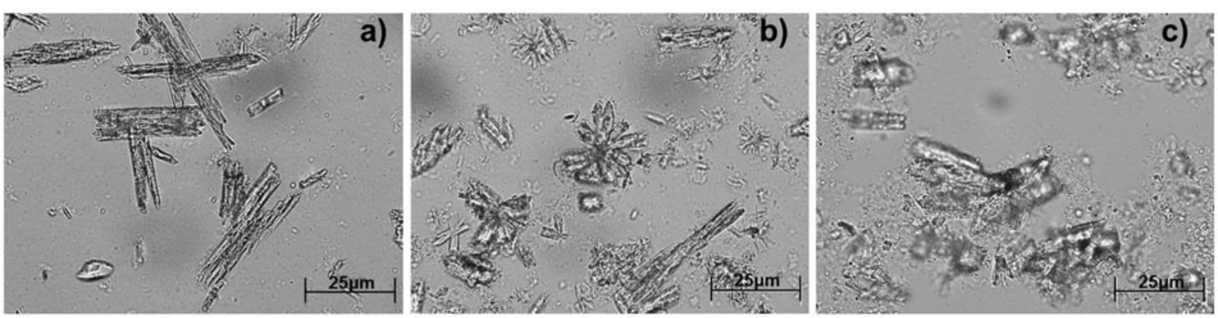

Fig. 4. MAP crystallization (400X, bar = 25 μm): (a) w/o seed, (b) w/ MAP seed and (c) w/zeolite seed.

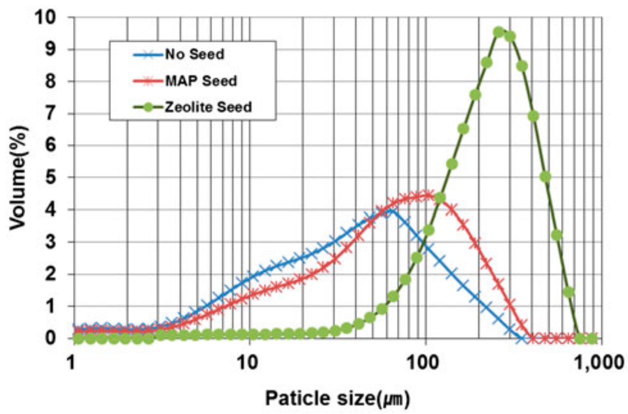

Fig. 5. Particle size distribution.

4. Conclusions

Struvite crystallization is an effective process to recover nutrients from anaerobically digested effluent of swine wastewater but requires the addition of magnesium from an external source. The results of all our experiments confirmed that seawater has substantial potential to be used as a magnesium source in the struvite crystallization process. The XRD results we obtained confirmed the crystal structure as struvite; therefore, the reject water from the seawater reverse osmosis process can be used as an alternative magnesium source. The removal efficiency for phosphate obtained by almost all the experiments was more than 90%. Injecting phosphate to adjust the molar ratio resulted in an increase in the removal efficiency for ammonia nitrogen. Experiments were conducted using natural zeolite to enhance the purity of the struvite and the crystal size, as seawater was used as a magnesium source. The seed materials were used successfully as nucleation sites. Using natural zeolite as an external seed resulted in superior performance compared with the synthesized struvite seed.

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