### Korean Journal of Environmental Agriculture

Korean J Environ Agric. 2023;42(2):83-92, https://doi.org/10.5338/KJEA.2023.42.2.11 Published online 27 April 2023, Printed 30 June 2023

**Research Article** 





Online ISSN: 2233-4173

## **Recovery of Ammonium Nitrogen and Phosphate from** the Piggerv Wastewater as Struvite and Its Assessment for the Reduction of Water Pollution Through the Field Test

Daeik Kim<sup>1</sup>, Sun Jin Hwang<sup>2</sup>, Su Ho Bae<sup>3</sup> and Keon Sang Ryoo<sup>4\*</sup>

<sup>1</sup>School of Electrical, Electronic Communication, and Computer Engineering, Chonnam National University, Yeosu 59626, Korea <sup>2</sup>Department of Environmental Science and Engineering, College of Engineering, Kyung Hee University, Yongin 17104, Korea <sup>3</sup>Department of Civil Engineering, Andong National University, Andong 36729, Korea

<sup>4</sup>Department of Chemical and Biological Engineering, Andong National University, Andong 36729, Korea

Received: 19 March 2023/ Revised: 4 April 2023/ Accepted: 20 April 2023

Copyright © 2023 The Korean Society of Environmental Agriculture

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

#### ORCID

Daeik Kim https://orcid.org/0009-0007-3426-4706

Sun Jin Hwang https://orcid.org/0000-0001-8262-5904

#### Abstract

Excess N and P from the livestock manure applied to farmlands, have entered the water systems and poses a serious threat to the natural environment. Consequently, there has been recent awareness towards the management of livestock manure and its related fields. In this study, piggery wastewater was collected from a piggery in Pohang city, Korea. At 800°C, thermal decomposition of a natural stone, magnesite (MgCO<sub>3</sub>), yielded powered MgO with particle sizes ranging between 10 to 100 µm. Furthermore,  $NH_4^+$ -N and  $PO_4^{3-}$ -P were recovered as struvite precipitates from the piggery wastewater, by adjusting the pH with MgO and H<sub>3</sub>PO<sub>4</sub>. At pH 10, the recovery efficiencies of  $NH_4^+$ -N and PO<sub>4</sub><sup>3-</sup>-P were found to be 86.1% and 94.1%, respectively. Using an X-ray Diffractometer (XRD), the struvite in the precipitate was confirmed to be consistent

\* Corresponding author: Keon Sang Ryoo Phone: +82-54-820-5453; Fax: +82-54-822-5452; E-mail: ksr@andong.ac.kr

Su Ho Bae https://orcid.org/0000-0002-9042-1284

Keon Sang Rvoo https://orcid.org/0000-0003-4346-6268

with standard pure struvite. Further, the purity of the struvite precipitate was analyzed using an energy dispersive X-ray (EDX) and thermal gravimetry-differential thermal analysis (TG-DTA), and found to be between 79.2% and 93.0%. Additionally, struvite-containing piggery wastewater and sawdust were mixed in a weight ratio of 2.5:1 and processed into a mature compost. The newly manufactured compost passed all quality standards required for first-class graded livestock composts. Moreover, this compost was sprayed directly onto the soil at the test site, and various parameters of the soil's effluent, such as total organic carbon (TOC), total nitrogen (T-N), total phosphorus (T-P), and dissolved oxygen (DO), were analyzed and measured. Based on these results, it is determined that the newly manufactured compost can more significantly reduce water pollution than commercial compost.

Key words: MgO, N, Newly-manufactured compost, NH<sub>4</sub><sup>+</sup> -N, P, PO<sub>4</sub><sup>3-</sup>-P, Struvite

#### Introduction

Consumption of meat in Korea is increasing rapidly every year because of the improvement of the income level of the people and, for that reason, livestock farms are also continuously expanding. However, the livestock manure is particularly recognized as a major obstacle to the continuous development of livestock industry due to the high concentration of nutrients such as nitrogen (N) and phosphorous (P) existing in it. These nutrients can cause eutrophication and dissolved oxygen depletion when they are present in excess in water bodies [1]. Therefore, environmental regulations related with livestock manure have been tightened to decrease the levels of nutrients entering into the water. For the past 20 years or so, many researchers have studied for removal and recovery of nutrients from livestock wastewater. For recovery of nutrients, a variety of methods such as adsorption, metal ion precipitation, biological process and etc. have been reported [2]. Among these methods, the biological process has known as the most common method to remove nutrients from livestock wastewater [3]. However, this method was not able to eliminate effectively nutrients from livestock wastewater due to the high content of nitrogen that has a toxic effect on microorganisms.

Recently, struvite precipitation has been widely applied to nutrients-rich wastewater treatments such as rare-earth wastewater. landfill leachate, coking wastewater. semi-conductor wastewater [4-12]. The crystal formation of struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) has the advantage of being able to recover ammonium nitrogen  $(NH_4^+-N)$  and phosphate  $(PO_4^{3-}-P)$  simultaneously. But despite strengths like the high recovery efficiency of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P, a fast reaction rate, and the ability to separate solids and liquids, this method has limitation in its widespread application due to the inadequate amount of Mg2+ in livestock wastewater required for the effective recovery. Therefore, the addition of external Mg<sup>2+</sup> source is required in the process of struvite crystallization, resulting in high operating costs [13]. To overcome this problem, many researchers have explored the low-cost materials consisting of Mg<sup>2+</sup> as magnesium source of struvite crystallization. The low-cost materials used as alternative of Mg<sup>2+</sup> source were brucite mineral, magnesite pyrolysate, magnesite mineral, and sea water [14-16]. Nevertheless, the use of the low-cost materials containing magnesium has not yet been evaluated in detail. Struvite precipitation

is greatly affected by pH and the stoichiometry ratio of  $Mg^{2+}$ ,  $NH_4^+$ , and  $PO_4^{3-}$ . Actually, the ideal pH for struvite precipitation is in the range of 8.0 and 10.0. And, the stoichiometry ratio of  $Mg^{2+}$ ,  $NH_4^+$  and  $PO_4^{3-}$ for struvite formation is usually 1:1:1 (Mg:NH4:PO4) [17]. However, the new struvite synthesis methods in which  $NH_4^+$  and  $PO_4^{3-}$  is deposited in the form of struvite crystals with a relatively low pH are not currently under study.

In general, livestock wastewater is perceived to be very difficult to convert to the compost because it emits a bad odor. However, by changing the above perception, there is a need to develop a technology that can produce livestock wastewater as a eco-friendly compost in order for a new source of income for livestock farmers. Struvite could be a viable and promising replacement for compost production because it has valuable nutrients such as phosphorous, nitrogen, potassium, which are a necessary element of crop cultivation, and being formed as massive deposits that are easy to collect and handle. Struvite dissolves very slowly when applied to soil, making it an attractive feature as slow-release compost for a long time. Several studies have been conducted for the production of struvite using human urine [18-21]. However, recent studies have focused only on the recovery of ammonium and phosphate as struvite, but its practical application in the field as compost has never been explored.

The major goal of this study is to recover NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P from piggery wastewater as a form of struvite. Magnesium oxide (MgO) was used as external Mg source in struvite precipitation. The effect of pH on the recovery efficiency of NH4+-N and PO43-P in piggery wastewater and the purity of obtained struvite were examined. The pH levels of piggery wastewater are generally between 8 and 9. But MgO, an additive, is not easily eluted as magnesium ions  $(Mg^{2+})$ in alkaline state. In addition, most phosphoric acids are present in the form of insoluble phosphoric acid in basic piggery wastewater. Hence, in this study, we tried to obtain the crystal structure of struvite under low acidic conditions. Finally, an on-site test was conducted on the effect of reducing water pollution using the newly-manufactured compost, which was prepared by mixing struvite-containing piggery wastewater and sawdust.

#### Materials and Methods

#### Materials and chemicals

The piggery wastewater used in this study was the wastewater from which solids are removed with a centrifuge dehydrator after collecting from a piggery livestock farm in Pohang city, Korea. MgO was in the form of powder with a particle size of 10 to 100  $\mu$ m after activating magnesite (MgCO<sub>3</sub>) natural stone for 1 h at 800°C by increasing to a temperature of 10°C/min. H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and NaOH were analytically pure and purchased from Merck (Darmstadt, Germany).

#### Removal of NH<sub>3</sub> and H<sub>2</sub>S

Removal rate of NH<sub>3</sub> and H<sub>2</sub>S from the piggery wastewater was measured by changing in the MgO dose. Here, the dose of MgO represents the relative amount of piggery wastewater. For this experiment, the batch reactor (storage scale of 1 ton) was made in a square shape, and an aeration device was installed inside. MgO is added to the piggery wastewater in the batch reactor. Since then, the content was aerated for 24 h by injecting air from the bottom using air pump. Soon after finishing the aeration, a fraction of piggery wastewater was collected in Tedlar bag. After spontaneous vaporization for 24 h, 100 mL gas was extracted from Tedlar bag and collected in an gas detection tube for analysis.

#### Recovery of NH4<sup>+</sup>-N and PO4<sup>3-</sup>-P as struvite

Studies on the recovery of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P in the piggery wastewater as struvite were performed by controlling pH. H<sub>2</sub>SO<sub>4</sub> and NaOH were used to adjust the pH of piggery wastewater. MgO and H<sub>3</sub>PO<sub>4</sub> were employed to recover NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P in the piggery wastewater as struvite. The mixture was agitated using a magnetic stirrer for 1 h at different pH from 5 to 11. After stabilizing the mixture for 30 min, the supernatant was filtered using glass microfiber filter (GF/ C, 47 mm) for component analysis. The obtained struvite precipitation was washed with deionized water several times and then dried in an oven at 35°C for 2 days. The dried precipitates were analyzed for the morphology and the purity of struvite.

#### Analytical methods

 $NH_3$  and  $H_2S$  were analyzed using an automated thermal desorber gas chromatograph/mass spectrometer (ATD-GC/MS, Clarus 690 GC, Clarus SQ8T, PerkinElmer, USA). Analysis of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P was performed by ultraviolet absorbance method and ascorbic acid reduction method at absorbance of 220 nm and 880 nm, respectively, using an ultravioletvisible spectrometer (UV/Vis, Cary-5000, Varian Technologies, USA). The concentration of Mg<sup>2+</sup> was quantified by using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Agilent 7800, Agilent Technologies, USA). The crystal structure of struvite was identified using a x-ray diffractometer (XRD, Ultima IV, Rigaku, Japan) with ICSD search program. The crystal shape and chemical composition of struvite were characterized through a field emission scanning electron microscope (FE-SEM, MYRA 3 XMH, Tescan, Czech) coupled with energy dispersive x-ray (EDX, X-MaxN, Oxford, UK). Thermal changes of struvite were analyzed at a temperature increase rate of 10°C/ min in a nitrogen atmosphere up to 800°C using a thermal gravimetry-differential thermal analysis (TG-DTA, 8122, Rigaku, Japan). The pH was measured by a pH meter (Radiometer, PHM 250 ion analyser, Woonsocket, RI, USA). Water samples (BOD, TOC, TSS, T-N, T-P, DO and EC) were analyzed according to the water pollution process test method in Korea.

#### Quality inspection of the newly-manufactures compost

To convert struvite-containing piggery wastewater into compost, the wooden structure was constructed with a size of 10 m<sup>2</sup>. Two tons of sawdust were placed in the structure, which was equipped with rain-shielding facilities and a rotary spray system to spray piggery wastewater from the top. Approximately a half ton of piggery wastewater a day was sprayed uniformly on the top of the sawdust 10 times through a spray system. Piggery wastewater slowly permeated into the sawdust as time goes on. The compost was turned upside down once a day using an excavator, dried and fermented. About 30 days later, the heat started to produce inside the compost. After the maturity of compost is completed, the quality test of the newly-manufactured compost was conducted on various analysis items such as organic matter, heavy metals, Escherichia coli, C/N ratio and etc.

# Field test for comparison of water pollution reduction using commercial compost and newly-manufactured compost

When there was no rainfall in April 2022, a 1000 m<sup>2</sup>

of agricultural land was roughly divided into three equal parts (each 330 m<sup>2</sup>) and five furrows were made on each land to allow the effluent to flow to the sampling point. 10 bags (20 kg per bag) of commercial compost and the newly-manufactured compost was evenly sprayed on each area, respectively. The rest of the area was not added any compost. After spraying compost on soil, the soil was homogenized using a rotary machine. A water sprinkler was placed in the center and water was continuously sprinkled until the soil was soaked with water. After a certain period of time (approximately 1 h), effluent was generated and began to flow along the furrow. Effluent was collected at each 5 sampling site 3 m from each boundary point and analyzed for water quality test items such as total suspended solids (TSS), total organic carbon (TOC), biochemical oxygen demand (BOD), total nitrogen (T-N), total phosphorous (T-P), dissolved oxygen (DO) and electrical conductivity (EC). Here, the analysis of the above sample items was performed according to the current water pollution process test method based on QA/QC.

#### **Results and Discussion**

#### Removal efficiency of NH<sub>3</sub> and H<sub>2</sub>S by MgO dose

Fig. 1 represents the removal efficiency (%) of  $NH_3$ and  $H_2S$  from the piggery wastewater according to the dose of MgO during the 24-hour aeration. As seen in Fig. 1, as the dose of MgO increased, removal efficiencies of  $NH_3$  and  $H_2S$  from piggery wastewater gradually increased. At MgO dose of 0.8 wt.%,  $NH_3$ 



Fig. 1. Removal efficiency of  $NH_3$  and  $H_2S$  from the piggery wastewater according to MgO dose (wt.%) during the aeration of 1 h.

and  $H_2S$  showed the removal efficiencies of 65% and 77%, respectively. This phenomenon is because pH increases as MgO dissolves in the piggery waste- water. When MgO was not added, the pH of piggery wastewater was 8.2. The pH of piggery wastewater was increased to 9.2 when the dose of MgO was raised to 0.8 wt.%. The increase in pH with the addition of MgO is based on the following equation (1).

$$MgO + H_2O \rightarrow Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^{-}$$
(1)

NH<sub>3</sub> has different solubility depending on the pH level. The higher the pH, NH<sub>3</sub> exists more in a gaseous state rather than in a salt state and is easily volatilized into the atmosphere [24]. In order to remove NH<sub>3</sub> and H<sub>2</sub>S, most of the existing livestock wastewater treatments evaporate NH<sub>3</sub> and H<sub>2</sub>S into the atmosphere for three to six months by simply injecting air. As a result, it emits constant malodor to the surrounding area for a long time. By contrast, in this study, NH<sub>3</sub> and H<sub>2</sub>S can be volatilized rapidly into the atmosphere during the aeration of only one to two days when MgO was added to piggery wastewater. In addition to this, ammonia remaining in the form of NH<sub>4</sub><sup>+</sup> is precipitated in the form of struvite with magnesium oxide and fixed as a complete livestock compost.

# Recovery of NH4<sup>+</sup>-N and PO4<sup>3-</sup>-P from the piggery wastewater

The concentrations of NH<sub>4</sub><sup>+</sup>-N, Mg<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>-P and pH value in the MgO-untreated piggery wastewater were 3.15 g  $L^{-1}$ , 0.001 g  $L^{-1}$  and 0.24 g  $L^{-1}$  and 8.2, respectively. After removing NH3 gas with MgO (0.8 wt.%), the residual concentrations of NH<sub>4</sub><sup>+</sup>-N, Mg<sup>2+</sup>, PO4<sup>3-</sup>-P and pH in the piggery wastewater were founded to be 2.46 g  $L^{-1}$ , 0.002 g  $L^{-1}$ , 0.24 g  $L^{-1}$  and 9.2, respectively. In terms of these concentrations, the piggery wastewater still includes negligible amount of Mg<sup>2+</sup> and a low concentration of PO<sub>4</sub><sup>3-</sup>-P compared to NH4<sup>+</sup>-N. Struvite is a white crystalline substance composed of ammonia, magnesium and phosphate in an equal molar ratio. Therefore, some magnesium and phosphate salts are required to be added in the piggery wastewater for the effective recovery of NH4<sup>+</sup>-N. In this study, in order to form of struvite crystals, the molar ratio of NH4+-N, Mg2+ and PO4--P in the piggery wastewater was made to be 1:1:1 by adding H<sub>3</sub>PO<sub>4</sub> and MgO.

The most important factor for effectively recovering  $NH_4^+$ -N and  $PO_4^{3-}$ -P in the crystalline form of struvite is pH control. H<sub>2</sub>SO<sub>4</sub> was added to adjust the initial pH of piggery wastewater to 5, and then the pH was gradually increased by adding NaOH. Most phosphoric acid exists in the form of insoluble phosphoric acid in basic piggery wastewater, so the amount of phosphoric acid ions dissolved in piggery wastewater is extremely small. Additionally, MgO is also difficult to dissolve into Mg<sup>2+</sup> ions in basic state. For these reasons, this study attempted to produce struvite by lowering the pH of piggery wastewater to 5. Experiments were performed at pH range of 5-11 with a reaction time of 1 h. At pH 5, three constitutional species were maintained in a molten state without the formation of precipitate. However, white precipitate, so-called struvite, began to created from pH 6. Fig. 2 represents the concentrations (g L<sup>-1</sup>) of NH<sub>4</sub><sup>+</sup>-N, Mg<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup>-P remaining in piggery wastewater according to changes in pH. As seen in Fig. 2, it is observed that the remaining concentrations of NH4+-N and PO43-P decreased rapidly with the increase of pH and reached 0.35 g L<sup>-1</sup> and 0.67 g L<sup>-1</sup> at pH 10, which showed 86.1% and 94.1% of recovery efficiencies, respectively.

Huang et al. reported that 80% of  $NH_4^+$ -N and 96% of  $PO_4^{3-}$ -P from piggery wastewater were achieved using struvite precipitation at a Mg:N:P molar ratio of 2.5:1:1.22 Li et al. demonstrated that a high recovery rate of phosphorous (> 98%) from actual black water was achieved by using active serpentine as the magnesium source for struvite precipitation [23]. In this study, the maximum recovery efficiencies of  $NH_4^+$ -N and  $PO_4^{3-}$ -P were obtained at PH 6, resulting in recovery efficiencies of 62.4% and 64.1%, respectively. From these results, it is disclosed that struvite precipitates

Fig. 2.  $\rm NH_4^+,~Mg^{2+}$  and  $\rm PO_4^{3-}$  concentrations (g  $\rm L^{-1})$  according to pH changes in the piggery wastewater.

consisting of  $NH_4^+$ ,  $Mg^{2+}$ , and  $PO_4^{3-}$ -P can be generated from slightly acidic of pH 6. Struvite precipitates from its constituent ions were produced by the following reaction (2):

$$Mg^{2+}(aq) + NH_{4}^{+}(aq) + PO_{4}^{3-}(aq) + 6H_{2}O$$
  

$$\rightarrow NH_{4}MgPO_{4} \cdot 6H_{2}O(s)$$
(2)

#### Morphology of precipitates

During the experiments, abundant white aggregation with large particles were formed in the piggery wastewater. The precipitates obtained at pH 6 were collected and characterized by SEM (Fig. 3). They appeared in a crystal structure of a plate type with a diameter of 20-50 um. However, the size of the crystals decreased 10-30 um when pH increased to 10, suggesting that the content of struvite in the precipitates reduced with increasing pH. Furthermore, if pH is above 11, no obvious crystal was observed and amorphous compounds accounted for the majority of the precipitates. At this condition, 95% of NH<sub>4</sub><sup>+</sup> can be converted to NH<sub>3</sub>, which cannot be precipitated by the formation of struvite [22].

Fig. 4 represents the XRD pattern for the precipitates obtained at pH 6. The peaks were perfectly matched with those of standard pure struvite crystal (ICSD Standard, PDF# 01-071-2089). On the whole, it was confirmed that the precipitates composed of ammonium, magnesium, and phosphate (NH<sub>4</sub>MgPO<sub>4</sub> · 6H<sub>2</sub>O), a struvite of structure. The line of the peak is sharp and the high peaks represent that the precipitate is a good crystalline substance. As a result, it is very likely that NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P were recovered as struvite by the treatment process.



Fig. 3. SEM image of struvite precipitate produced at pH 6.



Fig. 4. XRD pattern of precipitates produced in the piggery wastewater at pH 6.

#### The purity of struvite

Determination of struvite purity in the precipitates obtained at pH 6 was carried out using FE-SEM/EDX and TG-DTA. respectively. FE-SEM spectra representing elemental constituents of precipitates were given in Fig. 5. The spectra showed that precipitates consist mainly of O, Mg, and P as major elements, which was consistent with the elemental composition of struvite. Table 1 represents the weight and atomic percentages for the elemental composition of precipitates, quantified by EDX. According to the analysis of EDX, it was found that the precipitates consisted of 18.99% of Mg and 25.98% of P as weight %. When these figures are converted to molar ratio, the ratio is 0.93:1, indicating similar to the theoretical molar ratio (1:1) of struvite. EDX analysis of precipitates demonstrated that purity of struvite in precipitates was approximately 93%. The pattern of the TG-DTA analysis on the precipitates is shown in Fig. 6. As seen, when temperature reached 325°C, the mass reduction of precipitates was about 40.7%. Commonly, the theoretical mass loss for the formula (NH<sub>4</sub>MgPO<sub>4</sub>  $\cdot$  6H<sub>2</sub>O) is 51.4% at the same temperature. This figure is the sum of hydrate as 44.08% and NH<sub>3</sub> as 7.34%, respectively [25]. Previous study has shown that the ammonia and the hydrate during the thermal decomposition of struvite are lost simultaneously. Based on the data from TG-DTA, it was confirmed that the content of struvite in the precipitate is approximately 79.2%. Considering the values obtained from FE-SEM/EDS and TG-DTA comprehensively, it was seen that the purity of struvite in the precipitates reaches from a minimum of 79.2% to



Fig. 5. FE-SEM spectra of precipitate.

Table 1. The weight and atomic percentages for elemental composition of precipitate by EDX

Element	Weight (%)	Atomic (%)
О	53.76	67.05
Mg	18.99	15.58
Al	0.10	0.07
Si	0.00	0.00
Р	25.98	16.74
К	0.94	0.48
Ti	0.00	0.00
Mn	0.00	0.00
Fe	0.13	0.05
Cu	0.10	0.03
Zn	0.00	0.00
Total	100.00	100.00



Fig. 6. TG-DTA profile of precipitates with temperatures.

a maximum of 93.0%.

# Quality inspection of the newly-manufactured compost

Table 2 shows the quality inspection of new com-

	Analysis items	Standard criteria for livestock compost (first-grade basis)	Newly manufactured compost
Specifications	Organics (%)	above 33	39.37
	As (mg/kg)	less 45	undetected
	Cd (mg/kg)	less 5	undetected
Pernicious ingredients	Hg (mg/kg)	less 2	undetected
	Pb (mg/kg)	less 130	24.6
	Cr (mg/kg)	less 200	29.7
	Cu (mg/kg)	less 360	194.2
	Ni (mg/kg)	less 45	22.4
	Zn (mg/kg)	less 900	794.1
	Coliform bacillus (O157:H7)	undetected	undetected
	Salmonella	undetected	undetected
	C/N ratio	less 35	24.6
Other specifications	Salinity (%)	less 2.0	1.54
	Moisture (%)	less 55	52.4
	Maturity degree (comeback method)	Above maturity completion (70%)	Maturity completion (70%)
	Insoluble hydrochloric acid (%)	less 25	8.47

Table 2. Quality inspection of the newly-manufactured compost

post manufactured in this study. It was seen that the newly-manufactured compost has passed the standard criteria for analysis items required by livestock compost. Based on the results, it implies that the newly-manufactured compost has potential for widespread use in agriculture because it has abundant nutrients such as N and P, less heavy metals and C/N ratio, and does not contain pathogenic bacteria.

# Quantitative analysis of TSS, TOC, BOD, T-N and T-P in the effluent from the soils

Table 3 shows the results of analyzing TSS, TOC, BOD, T-N and T-P in the effluent from the soils, which were divided into untreated soil (US), soil treated with commercial compost (SCC) and the newlymanufactured compost (SMC). All measurements of effluent were performed in five times for each soil. The mean concentration values of TSS discharged from US, SCC and SMC were 579 mg  $L^{-1}$ , 585 mg  $L^{-1}$  and 634 mg L<sup>-1</sup>, respectively. When comparing the concentration difference between SCC and SMC with US, TSS concentration of SMC increased by 8.6% compared to SCC. It is assumed that the increase in TSS in effluent of SMC is caused by inorganic minerals added while composting. As for analysis of TOC, when SMC is compared with SCC, SMC was found to be reduced by 23.5% compared to SCC. In case of BOD, the concentration of BOD discharged from SMC showed a

33.2% decrease compared with SCC. For T-N, it was found that T-N from SMC was reduced by 16.2% in comparison with SCC. Analysis result of T-P showed that the average values of T-P for US, SCC and SMC were 3.95 mg  $L^{-1}$ , 14.0 mg  $L^{-1}$  and 7.28 mg  $L^{-1}$ , respectively. When the concentration of T-P from SMC is compared with SCC, T-P decreased by 48.0%. Consequently, when compost lacking magnesium is sprayed on farmland, nitrogen and phosphoric acid are easily dissolved in water and acts as a direct water pollution source. However, nitrogen and phosphorus synthesized by struvite crystals are not soluble in water and are mixed with the soil as a particle, causing a direct effect of reducing water pollution. Therefore, when considering the above analysis items comprehensively, it is noteworthy that the newly-manufactured compost can reduce water pollution to a high rate when the newly-manufactured compost is sprayed on the soil instead of commercial compost.

# Analysis of EC and DO from the effluent of the soils

The amounts of DO and EC of effluent discharged from each soil were analyzed in real time and their results were presented in Table 4. The values of EC measured in the effluent of US, SCC and SMC were 237 mg L<sup>-1</sup>, 628 mg L<sup>-1</sup> and 486 mg L<sup>-1</sup>, respectively. When spraying newly-manufactured compost on soil,

Analysis items		Spot					A	Chan dand danistics
		1	2	3	4	5	Average (mg L )	Standard deviation
	Untreated soil	561	597	637	516	582	579	44.69
TSS ( Newl	Commercial compost	648	613	587	546	531	585	47.94
	Newly manufactured compost	668	643	597	631	629	634	25.69
	Untreated soil	16.8	16.7	13.7	19.1	21.7	17.6	2.99
TOC	Commercial compost	91.6	97.1	103.4	89.7	110.7	98.5	8.66
	Newly manufactured compost	74.7	64.8	78.9	74.7	84.7	75.6	7.28
BOD C Newly	Untreated soil	14.4	16.4	17.2	14.3	16.9	15.8	1.39
	Commercial compost	84.7	76.4	82.4	77.9	94.2	83.1	7.04
	Newly manufactured compost	54.7	48.9	59.4	62.4	50.7	55.2	5.69
	Untreated soil	19.7	18.6	17.5	19.2	16.9	18.4	1.16
T-N Com Newly m	Commercial compost	32.7	35.5	38.9	32.4	29.6	33.8	3.53
	Newly manufactured compost	29.4	31.0	28.7	26.8	26.1	28.4	1.98
T-P	Untreated soil	3.81	4.12	3.84	3.96	4.01	3.95	0.13
	Commercial compost	12.6	13.4	15.8	13.4	14.8	14.0	1.28
	Newly manufactured compost	6.48	7.64	8.15	6.94	7.18	7.28	0.64

Table 3. Analysis of TSS, TOC, BOD, T-N and T-P in effluents from each soil

Table 4. Analysis of EC and DO for each soil

Analyzia itama	Spot				
Analysis hellis	Untreated soil	Commercial compost	Newly-manufactured compost		
EC (uS cm <sup>-1</sup> )	237	628	486		
DO (mg L <sup>-1</sup> )	3.6	0.8	2.1		

the pollution of water quality could be decreased by 36.3% compared to commercial compost. From the perspective of DO, it is judged that newly-manufactured compost can lower the concentration of DO by 46.4% than commercial compost.

#### Conclusion

In order to remove NH<sub>3</sub> and H<sub>2</sub>S, MgO (wt.%) was added into the piggery wastewater as a weight ratio of the piggery wastewater while aerating. When MgO is added by 0.8%, the removal efficiencies of NH<sub>3</sub> and H<sub>2</sub>S showed 65% and 77%, respectively, compared to the piggery wastewater untreated with MgO. The MgO used in this study increased the pH of the piggery wastewater, providing condition for removing NH<sub>3</sub> and H<sub>2</sub>S easily. NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P remaining in the piggery wastewater was recovered as the form of precipitate, referred as struvite. The molar ratio of NH<sub>4</sub><sup>+</sup>-N, Mg<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup>-P in piggery wastewater was made to be 1:1:1 by adding H<sub>3</sub>PO<sub>4</sub> and MgO. The struvite crystals were significantly influenced by pH. Hence, the pH of the piggery wastewater gradually increased from 5 to 11. Precipitates began to be produced from pH 6. At pH 10, recovery efficiencies of NH<sub>4</sub><sup>+</sup>-N and PO43-P were found to be 86.1% and 94.1%, respectively. Out of total recovery efficiency, the highest recovery efficiency was achieved at a weakly acidic of pH 6. The presence of struvite in the precipitate was examined by XRD, representing a good crystalline substance. Above pH 11, no obvious struvite crystals were observed and most of their presence existed in an amorphous form. The purity of struvite in the precipitate was measured by FE-SEM/EDX and TG-DTA, respectively. Based on the data obtained from above analytical instruments, it was assumed that the purity of struvite in the precipitate was between 79.2% and 93.0%. The new compost was manufactured by mixing struvite-containing piggery wastewater and sawdust at a weight ratio of 2.5:1. The newly-manufactured compost has passed the standard requirements such as organic content, heavy metals, C/N ratio, salinity, coliform bacillus and etc. for livestock compost. To evaluate the effectiveness of reducing water pollution by the newly-manufactured compost, the newly-manufactured compost was sprayed on the soil at the actual site and then the concentrations for TOC, BOD, T-N, T-P and DO in effluent of soil were compared with commercial compost. Through field test, it was confirmed that water pollution can be significantly reduced by the newly-manufactured compost rather than commercial compost.

#### Note

The authors declare no conflict of interest.

#### Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2022R1F1A1060823).

#### References

- Miroslav H, Pavel H, Josef B, Jarmila K (2021) Arsenic as acontaminant of struvite when recovering phosphorous from phosphogypsum wastewater. Journal of the Taiwan Institute of Chemical Engineers, 129, 91-96. https://doi.org/10.1016/j.jtice.2021.10.005.
- Anderson KB, Beukes JA, Feilberg A (2013) Nonthermal plasma for odour reduction from pig houses-A pilot scale investigation. Chemical Engineering Journal, 223, 638-646. https://doi.org/10.1016/j.cej. 2013.02.106.
- Zubair M, Wang S, Zhang P, Ye J, Liang J, Nabi M, Zhou Z, Tao X, Chen N, Sun K, Xiao J, Cai Y (2020) Biological nutrient removal and recovery from solid and liquid livestock manure: Recent advance and perspective. Bioresource Technology, 301, 122823. https:// doi.org/10.1016/j.biortech.2020.122823.
- Masindi V, Fosso-Kankeu E, Mamakoa E, Nkambule TTI, Mamba BB, Naushad M, Pandey S (2022) Emerging remediation potentially of struvite developed from municipal wastewater for the treatment of acid mine drainage. Environmental Research, 210, 112944. https:// doi.org/10.1016/j.envres.2022.112944.
- Wagner E, Karthikeyan G (2022) Preciping phosphorous as struvite from anaerobically-digested dairy manure. Journal of Cleaner Production, 339, 130675. https://doi.org/10.1016/j.jclepro.2022.130675.

- Zhou, Z, Hu D, Ren W, Jiang Y, Wang L (2015) Effect of humic sustances on phosphorous removal by struvite precipitation. Chemosphere, 141, 94-99. https:// doi.org/10.1016/j.chemosphere.2015.06.089.
- Wu H, Vaneeckhaute C (2022) Nutrient recovery from wastewater: A review on the integrated physicochemical technologies of ammonia stripping, adsorption and struvite precipitation. Chemical Engineering Journal, 433, 133664. https://doi.org/10.1016/j.cej.2021. 133664.
- Vasa TN, Chacko SP (2021) Recovery of struvite from wastewater as an eco-friendly fertilizer: Review of the art and perspective for a sustainable agriculture practice in India. Sustainable Energy Technologies and Assessments, 48, 101573. https://doi.org/10.1016/j. seta.2021.101573.
- Huang H, Jiang Y, Ding L (2014) Recovery and removal of ammonia-nitrogen and phosphate from swine wastewater by internal recycling of struvite chlorination product. Bioresource Technology, 172, 253-259. https://doi.org/10.1016/j.biortech.2014.09.024.
- Rech I, Kamaogawa MY, Jones DL, Pavinato PS (2020) Synthesis and characterization of struvite derived from poultry manure as a mineral fertilizer. Journal of Environmental Management, 272, 111072. https://doi.org/10.1016/j.jenvman.2020.111072.
- Krishnamoorthy N, Arunachalam T, Paramasivan B (2021) A comparative study of phosphorous recovery as struvite from cow and human urine. Materials Today: Proceedings, 47, 391-395. https://doi.org/10. 1016/j.matpr.2021.04.587.
- Tao W, Fattah KP, Huchzermeier MP (2016) Struvite recovery from anaerobically digested dairy manure: a review of application potential and hindrance. Journal of Environmental Management, 169, 46-57. https://doi.org/10.1016/j.jenvman.2015.12.006.
- Yilmazel YD, Demirer GN (2011) Removal and recovery of nutrients as struvite from anaerobic digestion residues of poultry manure. Environmental Technology, 32, 783-794. https://doi.org/10.1080/09593330. 2010.512925.
- 14. Lahav O, Telzhensky M, Zewuhn A, Gendel Y, Gerth J, Calmano W, Birnhack L (2013) Struvite recovery from municipal-wastewater sludge centrifuge supernatant using seawater NF concentrate as a cheap Mg(II) source. Separation and Purification Technology, 108, 103-110. https://doi.org/10.1016/j.seppur. 2013.02.002.
- 15. Merino-Jimenez I, Celorrio V, J. Fermin DJ, Greenman

J, Ieropoulos I (2017) Enhanced MFC powder production and struvite recovery by the addition of sea salts to urine. Water Research, 109, 46-53. https:// doi.org/10.1016/j.watres.2016.11.017.

- Ye Z, Shen Y, Ye X, Zhang Z, Chen S (2014) Phosphorous recovery from wastewater by struvite crystallization: Property of aggregates. Journal of Environmental Science, 26, 991-1000. https://dx.doi.org/ 10.1016/S1001-0742(13)60536-7.
- Chauhan CK, Joshi MJ (2013) In vitro crystallization, characterization and growth-inhibition study of urinary type struvite crystals. Journal of Crystal Growth, 362, 330-337. https://doi.org/10.1016/j.jcrysgro.20 11.11.008.
- Sathiasivan K, Ramaswamy J, Rajesh (2021) Struvite recovery from human urine in inverse fluidized bed reactor and evaluation of its fertilizing potential on the growth of Arachis hypogaea. Journal of Environmental Chemical Engineering, 9, 104965. https://doi. org/10.1016/j.jece.2020.104965.
- Ganrot Z, Dave G, Nilsson E (2007) Recovery of N and P from human urine by freezing, struvite precipitation, and adsorption to zeolite and active carbon. Bioresource Technology, 98, 3112-3121. https://doi. org/10.1016/j.biortech.2006.10.038.
- 20. Lind BB, Ban Z, Byden S (2000) Nutrient recovery

from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Bioresource Technology, 73(2), 169-174. https://doi. org/10.1016/S0960-8524(99)90157-8.

- Wei SP, van Rossum F, van de Pol GJ, Winkler MKH (2018) Recovery of phosphorous and nitrogen from human urine by struvite precipitation, air stripping and acid scrubbing: A pilot study. Chemosphere, 212, 1030-1037. https://doi.org/10.1016/j.chemosphere. 2018.08.154.
- Huang H, Xu C, Zhang W (2011) Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology. Bioresource Technology, 102, 2523-2528. https://doi.org/10.10 16/j.biortech.2010.11.054.
- 23. Li X, Zhao X, Zhang J, Hao J, Zhang Q (2022) Struvite crystallization by using active serpentine: An innovative application for the economical and efficient recovery of phosphorous from black water. Water Research, 221, 118678. https://doi.org/10.1016/j.wa tres.2022.118678.
- Polat S, Eral HB (2022) Effect of hyaluronic acid on the struvite crystallization: A structural, morphological, and thermal analysis study. Journal of Crystal Growth, 592, 126734. https://doi.org/10.1016/j.jcrys gro.2022.126734.