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Effect of organic matter on phosphorus recovery from sewage sludge subjected to microwave hybrid pretreatment

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ABSTRACT

Microwave (MW) hybrid processes are able to disrupt the flocculent structure of complex waste activated sludge, and help promote the recovery of phosphorus as struvite. In this study, to optimize struvite yield, (1) the characteristics of matter released in MW-hybrid treatments were compared, including MW, MW-acid, MW-alkali, MW-H₂O₂, and MW-H₂O₂-alkali. The results showed that selective release of carbon, nitrogen, phosphorus, Ca²⁺, and Mg²⁺ achieved by sludge pretreatment using MW-hybrid processes. MW-H₂O₂ is the recommended sludge pretreatment process for phosphorus recovery in the form of struvite. The ratio of Mg²⁺:NH₄⁺-N:PO₄³⁻-P was 1.2:2.9:1 in the supernatant. (2) To clarify the effects of organic matter on struvite recovery, the composition and molecular weight distribution of organic matters were analyzed. Low molecular weight COD was found to facilitate the removal rate of NH₄⁺-N and PO₄³⁻-P via crystallization, and the amorphous struvite crystals (<1 kDa) from the filtered solutions had high purity. Therefore, the present study reveals the necessity of taking into consideration the interference effect of high molecular weight organic matters during struvite crystallization from sewage sludge.

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Introduction

The amount of sludge produced by biological sewage treatment plants around the world has been constantly increasing. Thus, the treatment and disposal of excess sewage sludge are becoming a challenge for wastewater treatment plants (WWTPs). The challenges have been amplified by current legal constraints, land shortages, rising costs, and public sensitivity. For the purpose of preventing eutrophication, biological nutrient removal (BNR) technologies are used worldwide, wherein phosphorus is locked into the structure and polymers of the sewage sludge.

Phosphate-based fertilizers have helped spur agricultural gains over the past century. However, global phosphorus resources have been rapidly depleted (Gilbert, 2009), and prices continue to soar as this commodity shortage worsens. The phosphorus content of sludge, due to the application of BNR processes, ranges between 4% and 9% (Barlindhaug and Odegaard, 1996). Sewage and sludge are the main channels for phosphorus loss to the environment. Therefore, phosphate recovery from sewage sludge could provide a key solution to the phosphate shortage.

One of the main obstacles for sludge reduction and resource recovery is that the complex organic materials that

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make up cell walls and membranes protect intracellular materials from biodegradation. In recent studies, sludge pretreatment processes have been of great interest for the release of organic matter, nitrogen, and phosphorus, in order to enhance the anaerobic digestibility of waste activated sludge (WAS) for biogas production. These pretreatment methods also aid the recovery of phosphorus in appropriate forms from WAS (Wong et al., 2006b).

As a promising sludge pretreatment technology, microwave (MW) hybrid pre-treatment is able to disrupt the flocculent structure of complex waste activated sludge (Xiao et al., 2012), which is a key issue for most sludge 3R (reduce, reuse, and recycle) technologies.

MW and hybrid sludge pretreatment techniques (e.g., MW with pressure) have gained popularity due to the ease of their control and high efficiency. Methods such as MW-acid and MW-alkali (Cheng et al., 2009), MW-H₂O₂ (Wong et al., 2006a), and MW coupled with an advanced oxidation process (AOP) have been used to improve sludge dissolution and disinfection. Current studies on sludge pretreatment for sludge reduction have mainly addressed the issues of particle size distribution and the release efficiencies of carbon, nitrogen, and phosphorus (Wang et al., 2015).

Struvite precipitation is an ideal phosphorus recovery technique for sludge because struvite (magnesium ammonium phosphate) is an excellent slow-release fertilizer (Ye et al., 2014). Phosphorus recovery in the form of struvite has earned recognition owing to its technical feasibility and economic viability (Guadie et al., 2014). Sludge pretreatment is designed to maximize the release of organic release simultaneous with NH₄⁺-N, PO₄³⁻-P, and Mg²⁺, which could reduce the chemical costs of struvite recovery.

The main factors governing struvite crystallization are the initial reaction parameters (e.g., pH, ionic strength, ionic ratio) (Doyle and Parsons, 2002), and the operating parameters (e.g., initial temperature, reaction time, stirring intensity) (Stratful et al., 2001). Although many methods (e.g., mechanical, heat, chemical, and hybrid technologies) have been applied to rupture sludge particles and recover phosphorus (Bi et al., 2014), few studies have considered the effect of organic matter on this process. In a previous study, it was found that organic matters with molecular weight (MWt) < 8 kDa acted as a trigger for recover struvite in cat urine (Matsumoto and Funaba, 2008). These authors proposed that a substance of the proper MWt could enhance struvite recovery after sludge pretreatment. However, for pretreated sludge, there are few studies focused on the effects of organic matter on struvite crystallization during phosphorus recovery. Knowledge about the molecular weight distribution (MWtD) of treated sludge is required for its further utilization, but this has not received particular attention. Additionally, the effect of the organic-particle size distribution on the recovery of phosphorus as struvite after WAS pretreatment is still unknown. Furthermore, to date, there has been no research focused on the effect of MW-hybrid sludge treatments on the evaluation of organic matter release characteristics, such as their influence on the MWtD of the organics, or subsequent effects on struvite recovery from sludge.

This study had two goals: The first goal was to investigate the characteristics of sludge disintegration that resulted from

MW-hybrid treatments (i.e., MW, MW-acid, MW-alkali, MW-H₂O₂, and MW-H₂O₂-alkali). These characteristics would first be evaluated in terms of the release of carbon, nitrogen, phosphorus, calcium, and magnesium. They would also be evaluated in terms of the MWtD of the proteins, sugars, and other organics released. The second goal was to investigate the effects of the MWtD of the organic matter in the pretreated sludge on struvite crystallization, to optimize struvite yield and purity.

1. Materials and methods

1.1. Sludge pretreatment by MW-hybrid processes

Sludge was collected at a wastewater treatment station in Beijing, passed through a 60-mesh screen, then adjusted to a concentration of about 20 g/L of mixed liquor suspended solids (MLSS) for batch tests. The WAS characteristics were as follows: MLSS was 18.96 ± 0.17 g/L, mixed liquor volatile suspended solids (MLVSS) 11.43 ± 0.11 g/L, total chemical oxygen demand (TCOD) 19.21 ± 0.12 g/L, total phosphorus (TP) 0.58 ± 0.05 g/L, total nitrogen (TN) 0.80 ± 0.02 g/L, and pH was 7.29 ± 0.03 .

The operational parameters used for sludge pretreatment with the MW-hybrid processes are listed in Table 1 (Wang et al., 2015). One-liter concentrated sludge samples (20 g/L) were treated using MW irradiation. Details of the microwave oven (2450 GHz, 1000 W; Julong, China) were described previously (Wang et al., 2009).

1.2. Molecular weight distribution of organic matter in the supernatant

The organic matter in the sludge supernatant mainly consisted of proteins, sugars, and organic acids after microwave pretreatment (Mehdizadeh et al., 2013). The MWtD of the organic matter is influenced by the types of pretreatment and by the operation parameters. The filtration method successfully separated the organic matter for examination of

Table 1 – Operational parameters of sludge pretreatment by microwave hybrid processes.

Processes	Methods of sludge pretreatment
MW	Sludge was heated directly to 100°C with microwave (MW) irradiation.
MW-acid	The sludge pH was adjusted to 2.5 using a 5.0 mol/L HCl solution, and then treated with MW.
MW-alkali	The sludge pH was adjusted to 10.0 using a 5.0 mol/L NaOH solution, and then treated with MW.
MW-H ₂ O ₂	The sludge was heated to 80°C with MW irradiation, then H ₂ O ₂ was added at a ratio of H ₂ O ₂ :MLSS ^a = 0.2, with continued heating to 100°C by MW irradiation.
MW-alkali-H ₂ O ₂	The sludge pH was adjusted to 10.0 using a 5.0 N NaOH solution, and then treated as with the MW-H ₂ O ₂ treatment.

^a Mixed liquor suspended solids; Source: Wang et al., 2015.

its crystallization. Thus, regenerated cellulose ultrafiltration (UF) membranes in a 200 mL Millipore 8200 stirred Amicon cell (Millipore Co., USA) were used in this study. Membranes with MWt cutoffs (MwC) of 100, 30, 10, 5, 3, and 1 kDa were arranged in a cascading series. The UF procedure was as follows (Eskicioglu et al., 2006). After rinsing the stirred cell, it was loaded with 180 mL of primary filtered (0.45 μm) and diluted (5:1) supernatants from sludge pretreated with MW, MW-acid, MW-alkali, MW-H₂O₂, and MW-alkali-H₂O₂. The concentration factor (the ratio of initial volume to retentate volume) was set at 6.0. Sufficient volumes of retentate and permeate were collected from each of the different MwC membranes (Fig. S1). For permeate and retentate, each MwC of the UF was analyzed, and the results were expressed in terms of percentage (w/w) of the SCOD, S-proteins (soluble-proteins), and S-sugars (soluble-sugars). The recovery rates of UF were more than 90% (Table S2).

1.3. Struvite crystallization

The preferred MW sludge pretreatment process for struvite crystallization was selected according to the following parameters: the release of carbon, nitrogen, phosphorus, calcium, and magnesium, as well as the ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$. The unfiltered supernatant (S_{RAW}), filtrate of the 0.45 μm microfiltration membrane (S_{MF}), filtrate of membranes with MwC of 10 kDa ($S_{10\text{K}}$), and filtrate of membranes with MwC of 1 kDa ($S_{1\text{K}}$); were used to recover struvite crystals. Two synthetic solutions ($S_{\text{-Ca}}$ and $S_{\text{+Ca}}$), prepared using NH_4Cl (0.05 mol), KH_2PO_4 (0.05 mol), and MgCl_2 (0.1 mol) solutions, were used as controls during the struvite crystallization experiments. The $S_{\text{+Ca}}$ solution contained an additional 0.1 mol Ca^{2+} (CaCl_2).

Struvite crystallization has been found to achieve better results at pH 8.5–10.0, Mg:P ratios of 1–2.5, and N:P ratios > 1 (Jaffer et al., 2002). The purity of struvite was improved by increasing the concentration of NH_4^+ remaining after crystallization (Doyle and Parsons, 2002). Therefore, the ratio of Mg:P was set at '2' by adding 0.05 mol MgCl_2 solution, and maintaining the reaction solution at pH 9.7 ± 0.2 . In addition, the ion losses from solution caused by ultrafiltration were replenished by the addition of NH_4Cl (0.05 mol), KH_2PO_4 (0.05 mol), MgCl_2 (0.1 mol), and CaCl_2 (0.1 mol) solutions. The final ion concentrations in the reaction solutions before struvite crystallization were 102.5 mg/L $\text{NH}_4^+\text{-N}$, 74.6 mg/L, $\text{PO}_4^{3-}\text{-P}$, and 115.5 mg/L Mg^{2+} in all samples (S_{RAW} , S_{MF} , $S_{10\text{K}}$, $S_{1\text{K}}$, $S_{\text{-Ca}}$, and $S_{\text{+Ca}}$). A concentration of 102.6 mg/L of Ca^{2+} was calculated for all samples except sample $S_{\text{-Ca}}$. The PHREEQC model (version 3; Parkhurst and Appelo, 2013) was used to simulate the precipitation process.

For MW-treated sludge, the sludge temperature was cooled from > 90°C to 50°C following filtration and free settling for solid-liquid separation. The temperature of struvite crystallization in this study was set at $(50 \pm 1)^\circ\text{C}$ for residual heat utilization in the next step of treatment (i.e., anaerobic fermentation), because temperature has little effect on struvite crystallization. The reaction time of struvite crystallization in this study was set at 20 min with a stirring rate of 500 ± 10 rpm through the use of magnetic stirring (Jaffer et al., 2002; Stratful et al., 2001).

1.4. Analysis

TCOD, SCOD, TSS (total suspended solids), and VSS (volatile suspended solids) were determined using standard methods (China EPA, 2002). NH_4^+ , total nitrogen (TN), $\text{PO}_4^{3-}\text{-P}$, and total phosphorus (TP) were determined using a SmartChem 200 Discrete Analyzer (AMS, France). Mg^{2+} and Ca^{2+} were analyzed using an inductively coupled plasma optical emission spectrometry (ULTIMA 2 ICP-OES, France). Sugars and proteins in solution were determined according to the Dubois and Lowry methods (Mehdizadeh et al., 2013). Sludge capillary suction time (CST) was determined using a Triton Type 304 M CST (Triton Electronics, UK). Sludge particle size was determined using a Malvern Mastersizer 2000 (Malvern, UK). Morphological and component analysis of the crystals were conducted with an S-3000 scanning electron microscope (SEM; Hitachi, Japan) and an S-3000 X-ray spectrum analyzer (Hitachi, Japan), respectively.

2. Results and discussion

2.1. Release of organic matter

As sludge was disrupted in all MW-hybrid pretreatments, extracellular polysaccharides and intracellular substances (cell fragments, proteins, and sugars) were released into the liquid, and were represented by total COD (Fig. 1). The COD concentrations in the supernatant of sludge pretreated by MW-alkali-H₂O₂, MW-H₂O₂, and MW-alkali were much higher (6660, 4725, and 6030 mg/L, respectively), than those observed for the MW and MW-acid treatments. The relative release rate of SCOD was 18.8%, which agrees with a previous report of 15% to 21% (Wang et al., 2015).

The release of proteins/S-proteins and sugars/S-sugars presented similar trends (Fig. 1). MW-acid treatment did not perform as well as MW-H₂O₂ or MW-alkali-H₂O₂. Interestingly, MW-alkali pretreatment performed as well for total organic

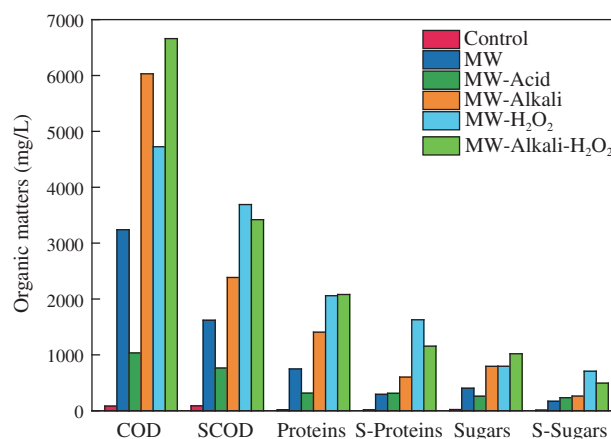


Fig. 1 – Release characteristics of chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), proteins, soluble proteins (S-proteins), sugars, and soluble sugars (S-sugars).

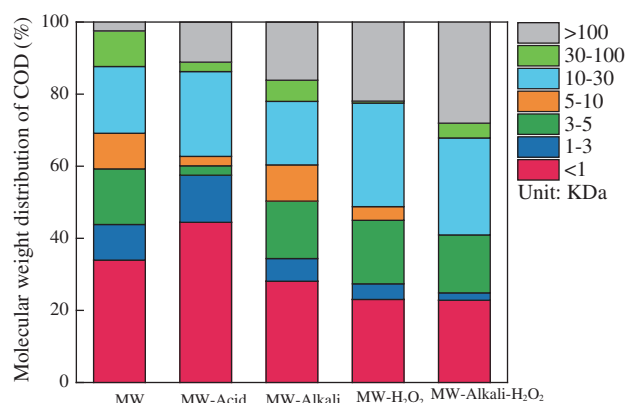


Fig. 2 – Molecular weight distribution of organic matter (represented by SCOD) from sludge pretreated by microwave MW, MW-acid, MW-alkali, MW-H₂O₂, and MW-alkali-H₂O₂ hybrid pretreatment processes.

matter, proteins, and sugars as the two MW with H₂O₂ groups, but performed as badly as the MW and MW-acid treatments in terms of soluble materials. This indicates that the alkali reacts with the cell walls and membranes, making them soluble in a variety of ways. In the release reaction, saponification occurred between alkali and the fatty acids of the cell membranes, changing their permeability, and damaging the cell walls or membrane structure. Therefore, adding alkali can promote the breakdown of organic structures in the sludge and increase the release of particulate organic matter. However, most of the particulate organic matter could not be further hydrolyzed to soluble phases, due to its durable structure or to the short reaction time.

2.1.1. Molecular weight distribution of organic matter

The MWtD of organic matter released was strongly affected by the type of pretreatment method used (Fig. 2). The MWtDs of MW-alkali, MW-H₂O₂, and MW-alkali-H₂O₂ were evenly distributed in four sets: <1 kDa; 3–5 kDa; 10–30 kDa; and >100 kDa. Low MWt organics were generated by release and secondary hydrolysis of the proteins by alkali, and by the oxidative decomposition of proteins and sugars. Generally, the MWt of cell-wall fragments, and of extra- and intra-cellular polymers, is >100 kDa. For sludge pretreated by MW, MW-acid, MW-alkali, MW-H₂O₂, and MW-alkali-H₂O₂, the organic materials affecting SCOD, with MWt >100 kDa, were 2.5, 11.1, 16.1, 22.0, and 28.1%, respectively. This indicates that the destruction of sludge structures and cell walls was successfully increased by these pretreatments, in the order given.

The SCOD-affecting organics with MWt < 1 kDa accounted for large proportions (34.0%, 44.4%, 28.1%, 23.0%, and 22.8%, respectively, for the pretreatments listed above). These were assumed to mainly be organic acids (Barker et al., 1999), which led to the decrease of pH.

For sludge pretreated by MW-hybrid processes, the portions of S-proteins with MWt fraction <5 kDa were similar, but those 5–100 kDa fractions differed (Fig. S2). For sludge pretreated by MW and MW-acid, most of the S-proteins were 5–30 kDa (46.8% and 53.4%, respectively); for sludge pretreated by MW-H₂O₂ and MW-alkali-H₂O₂, most of the S-proteins

appeared to be within the MWt range of 10–30 kDa (41.4% and 34.0%, respectively). For sludge pretreated by MW-alkali, most of the S-proteins appeared to be in the MWt range of 5–10 kDa (24.0%) and 30–100 kDa (20.8%). Pretreatment using MW-alkali, MW-H₂O₂, and MW-alkali-H₂O₂ can effectively release S-proteins from sludge, and then hydrolyze them to low MWt organics.

The high-MWt proteins were only hydrolyzed to proteins of 30–100 kDa by MW-alkali, but with pretreatment by MW-H₂O₂ and MW-alkali-H₂O₂, they were further hydrolyzed to proteins of 10–30 kDa. Similarly, the largest fraction of S-sugar molecules was 10–30 kDa in all pretreatments (Fig. S2), and the next largest fraction was of particles >100 kDa. This showed that the hydrolysis of sugars was difficult even in the presence of alkali and/or H₂O₂, because the peptidoglycan material making up bacterial cell walls is durable (Thibault, 2006), so that the sugars in many cells remained inaccessible.

As a separation method, the UF exhibited high reliability, although the interception and adsorption of the organics may be affected by factors such as temperature, pH, ionic strength, molecular structure, and trans-membrane pressure (Eskicioglu et al., 2006; Kuo and Parkin, 1996). In general, all the recovery values in this study were satisfactory (Table S1). The recovery rates from all samples were within the range 91.5%–107.4% for SCOD, S-proteins, NH₄⁺-N, and PO₄³⁻-P. The lowest recovery rate was 85.2%, for S-sugars in the group treated by MW-alkali-H₂O₂.

2.2. Release of nitrogen, phosphorus, calcium, and magnesium

Nitrogen and phosphorus were released along with organics during sludge lysis; however, the release patterns of NH₄⁺-N, soluble total nitrogen (STN), and total nitrogen (TN); PO₄³⁻-P, soluble total phosphorus (STP) and TP, were different (Fig. 3). The MW-acid process was the most efficient for releasing PO₄³⁻-P, STP, and TP. Two other pretreatments, MW-H₂O₂ and MW-alkali, were preferable for the release of NH₄⁺-N, with relative release rates of 11.3% and 9.4%, respectively. The results showed that addition of acid and/or H₂O₂ facilitated the release of NH₄⁺-N and PO₄³⁻-P, whereas the addition of alkali was disadvantageous for the release of NH₄⁺-N. Actually, alkali could improve the permeability of cell membranes (Erdinciler and Vesilind, 2000), making it easier for both NH₄⁺-N

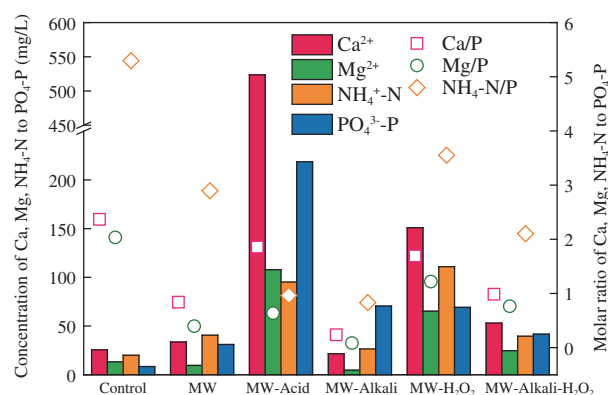


Fig. 3 – Concentration of Ca²⁺ and Mg²⁺ in sludge supernatant, and molar ratios of NH₄⁺-N: PO₄³⁻-P and Mg²⁺: PO₄³⁻-P in sludge supernatant; MW = microwave.

and $\text{PO}_4^{3-}\text{-P}$ to be released. However, at high pH and temperature, most of the $\text{NH}_4^+\text{-N}$ released formed NH_3 , and quickly evaporated into the air. Up to 99.68% of the nitrogen was in the form of NH_3 at pH 10 and 100°C , which was verified by the PHREEQC model. Additionally, at high pH, part of the phosphorus may be in the form of precipitates, causing high release of TP, but low release of $\text{PO}_4^{3-}\text{-P}$.

For the release of Mg^{2+} and Ca^{2+} , the MW-acid process was the most efficient pretreatment (Fig. 3), leaving concentrations of 107.9 and 523.6 mg/L of Mg^{2+} and Ca^{2+} respectively in the sludge supernatant after pretreatment. The next most effective pretreatment was the MW- H_2O_2 process, with Mg^{2+} and Ca^{2+} concentrations of 65.2 and 150.9 mg/L, respectively. After MW-hybrid pretreatment, Mg^{2+} , $\text{NH}_4^+\text{-N}$, and $\text{PO}_4^{3-}\text{-P}$ were simultaneously released from the sludge, reducing the cost of chemicals used to release Mg^{2+} for struvite precipitation.

2.3. Process selection for struvite crystallization

MW-hybrid processes were efficient for the release of carbon, nitrogen, and phosphorus, but the relative ratios were very different. MW-acid performed best for $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ release, but poorly for organics release. MW- H_2O_2 was efficient for the release of $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, SCOD, S-proteins, and S-sugars, which was beneficial for follow-up treatments such as sludge reduction and nutrient recovery. For sludge reduction, MW- H_2O_2 , MW-alkali, and MW- H_2O_2 -alkali were preferable due to their high release efficiency for soluble organics. For sludge reduction and nutrient recovery, MW- H_2O_2 was preferable for the high release efficiency for both organics and nutrients ($\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$), and for its improved solid-liquid separation after sludge pretreatment.

Phosphorus recovery through struvite crystallization is technically and economically feasible (Shu et al., 2006). The struvite formation reaction can be expressed as follows:



The solubility of struvite crystals is negatively related to the struvite activity product (SAP; $[\text{Mg}^{2+}] \times [\text{NH}_4^+] \times [\text{PO}_4^{3-}]$) (Matsumoto and Funaba, 2008). From Eq. (1), the ratio of $\text{Mg}^{2+}:\text{NH}_4^+\text{-N}:\text{PO}_4^{3-}\text{-P}$ is 1:1:1; in practice, struvite crystallization was better when the ratio of Mg:P was 1–2.5, and the N:P ratio was >1 (Jaffer et al., 2002). The purity of the struvite increased with higher NH_4^+ concentration remaining after crystallization (Doyle and Parsons, 2002). The $\text{Mg}^{2+}:\text{NH}_4^+\text{-N}:\text{PO}_4^{3-}\text{-P}$ ratio was 1.2:2.9:1 in the supernatant after sludge was pretreated with MW- H_2O_2 (Fig. S4). This further indicated that MW- H_2O_2 was preferable for struvite recovery.

The pH affects the concentration of the sludge constituents. Lowering the pH results in a decrease in the phosphorus concentration present as PO_4^{3-} , which is proportionately greater than the increase in the NH_4^+ concentration (Matsumoto and Funaba, 2008). Additionally, the pH of sludge pretreated by MW- H_2O_2 was 5.72, which not only prevents crystallization during sludge pretreatment, but also prevents scaling of the membrane surface during the follow-up membrane separation. Importantly, at pH 5.72, more than 80% of the carbon ($\text{CO}_3^{2-}/\text{HCO}_3^-/\text{CO}_2$) in the supernatant was in the form of CO_2 , and about 20% was HCO_3^- . There was almost no CO_3^{2-} , which effectively

avoided CaCO_3 precipitation. For phosphorus recovery as struvite, Ca^{2+} release was unfavorable. This is because calcium phosphate can be crystallized under certain conditions (such as when $\text{NH}_4^+\text{-N}$ is insufficient), which affects the purity of the struvite. Therefore, we chose MW- H_2O_2 pretreatment technology for phosphorus recovery via struvite crystallization. After filtration, the COD values in the initial sample solutions for struvite recovery were 4890 mg/L (S_{raw}), 3360 mg/L (S_{MF}), 2310 mg/L ($S_{10\text{K}}$), and 1560 mg/L ($S_{1\text{K}}$). In addition, the concentrations of $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, Ca, and Mg are shown in Fig. 3, where the ratio of $\text{NH}_4^+\text{-P}$ is 2.87–3.04 and that of Mg:P is 0.60–0.73.

2.4. Impacts of organic matter on phosphorus recovery

The formation and growth of struvite crystals are not determined solely by SAP. Several organic compounds, including proteins and glycosaminoglycan, modulate the growth of struvite crystals in urine (Matsumoto and Funaba, 2008). To investigate the effect of the MWt of organic matter on struvite crystallization, the organic matter was fractionated using a series of membranes. COD in the unfiltered solution (S_{RAW}) decreased from 4890 mg/L to 3360 mg/L (S_{MF}), 2310 ($S_{10\text{K}}$), and 1560 ($S_{1\text{K}}$), after passing through the 0.45 μm , 10 kDa, and 1 kDa membranes, respectively. The concentrations of $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, Mg^{2+} , and Ca^{2+} decreased slightly after filtration, and the ratios of N:P, Mg:P, and Ca:P were within the ranges of 2.9–3.0, 0.61–0.73, and 0.92–1.14, respectively (Fig. 4).

The removal rates of $\text{NH}_4^+\text{-N}$ from the four solutions (S_{RAW} , S_{MF} , $S_{10\text{K}}$, and $S_{1\text{K}}$) were 76.72%, 77.32%, 83.69%, and 89.99%, respectively, and those of $\text{PO}_4^{3-}\text{-P}$ were 94.62%, 98.69%, 99.21%, and 99.60%, respectively. The removal of both $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ increased when COD and MWt were decreased by filtration.

These results indicate that struvite crystallization was affected by organics, especially high-MWt organics (> 10 kDa), and that some organics were coated on the crystals by co-precipitation, which affected the purity of the struvite product. The removal rate of $\text{NH}_4^+\text{-N}$ from the $\text{C}_{-\text{Ca}}$ solution (without Ca^{2+}) was higher than that from the $\text{C}_{+\text{Ca}}$ solution (with Ca^{2+}). In contrast, the removal rate of $\text{PO}_4^{3-}\text{-P}$ from the $\text{C}_{-\text{Ca}}$ solution (85.45%) was lower than that from the $\text{C}_{+\text{Ca}}$ solution (98.16%). This indicates that $\text{PO}_4^{3-}\text{-P}$ competition occurred Ca^{2+} and Mg^{2+} , and that the crystallized product was partly calcium phosphate. The removal rates of Mg^{2+} and Ca^{2+} were also affected by organics, and the impact was more significant in the presence of low-MWt organics. (In this study, low concentrations of organic matter corresponded to low-MWt organics, such as organic acids). The complexation of metallic cations and organic acids is known to occur under certain conditions (Iskrenova-Tchoukova et al., 2010). This would lead to removal rates of Ca^{2+} and Mg^{2+} in the $S_{1\text{K}}$ solution being much higher than in the S_{RAW} , S_{MF} , and $S_{10\text{K}}$ solutions. However, the removal rates of Ca^{2+} and Mg^{2+} in the simulated solutions ($\text{C}_{-\text{Ca}}$ and $\text{C}_{+\text{Ca}}$) were much higher than those in $S_{1\text{K}}$.

2.5. Precipitant characteristics

For further investigation of the effects of organics on struvite crystallization, the crystalline morphology and elemental

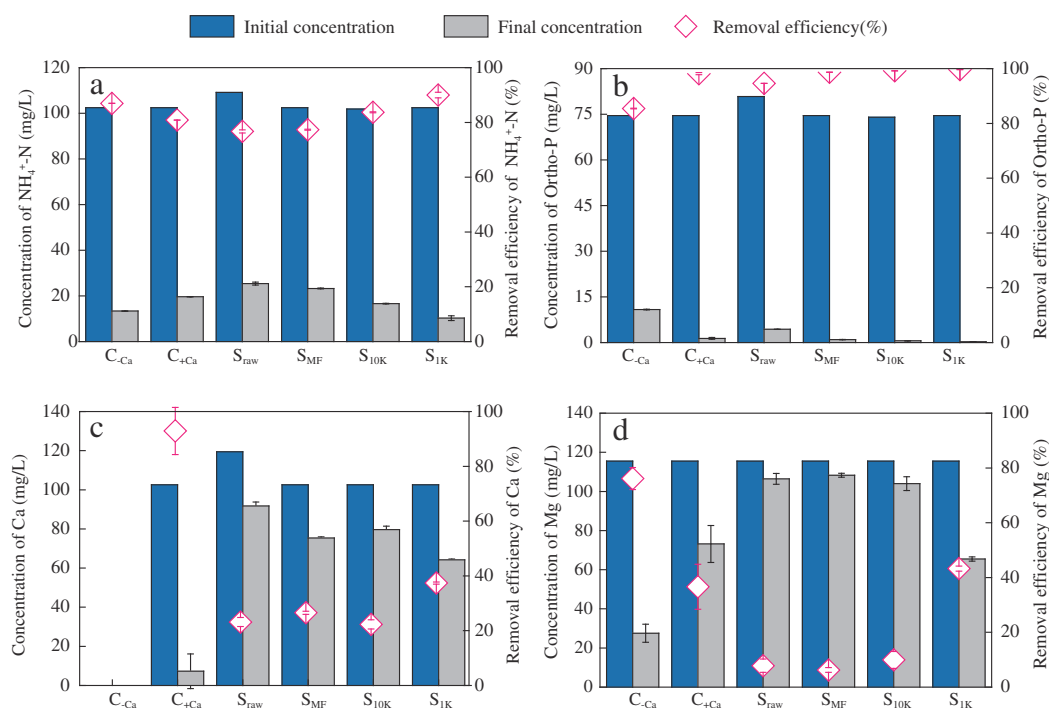


Fig. 4 – Profiles of ion variation before and after crystallization, for ammonium–nitrogen ($\text{NH}_4^+\text{-N}$), $\text{PO}_4^{3-}\text{-P}$, Mg^{2+} , and Ca^{2+} .

composition were determined using an SEM and energy spectrum analysis, respectively. The N:Mg:P ratio of the crystalline material was 0.84:1.7:1 in $\text{C}_{\text{-Ca}}$ (mole ratio), and was 0.67:1.15:1 for the $\text{C}_{+\text{Ca}}$ sample. This indicates that other precipitates, such as magnesium phosphate, were generated rather than struvite. Additionally, the ratio of Mg:P in $\text{C}_{+\text{Ca}}$ was lower than in $\text{C}_{\text{-Ca}}$, due to the $\text{PO}_4^{3-}\text{-P}$ competition between Ca^{2+} and Mg^{2+} . Consequently, the crystal morphology changed from polyhedral to amorphous (Fig. 5a and b), because of the presence of Ca^{2+} in the $\text{C}_{+\text{Ca}}$ sample.

Calcium phosphate was present in the product due to the high concentration of Ca^{2+} in solution. Although the SCOD of the $\text{S}_{10\text{K}}$ solution was 2190 mg/L (much higher than for the $\text{S}_{1\text{K}}$ solution: 1545 mg/L), their components of their precipitates were quite similar (Fig. 5e and f). The crystal morphology in solution was determined to be amorphous by direct observation, with the exception of the S_{RAW} (unfiltered) solution, indicating a significant effect of the seeding material on crystal morphology. In the presence of a seed material, nucleation can occur on the seed surface, which might influence crystal

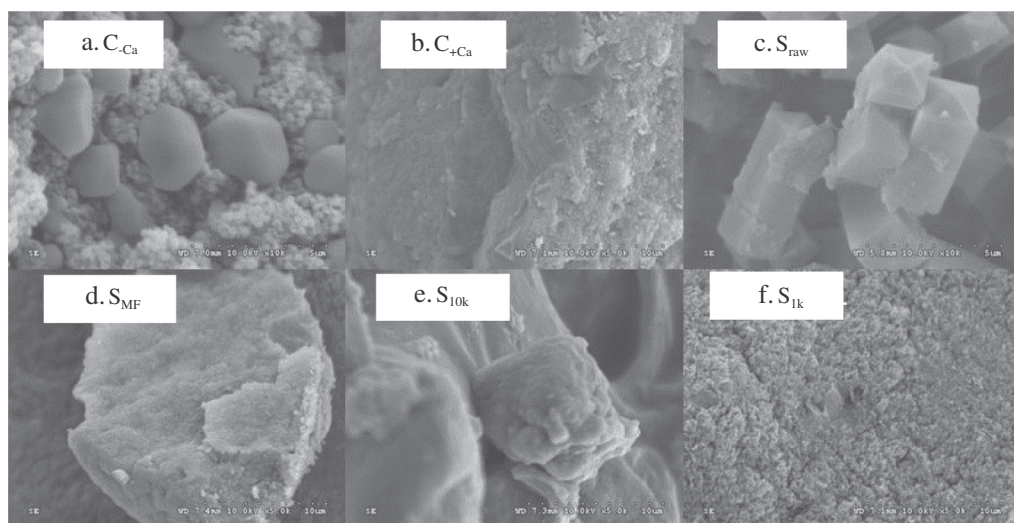


Fig. 5 – SEM images of crystal morphology at 5000 \times magnification. Products from: (a) Simulated solution without Ca^{2+} ($\text{C}_{\text{-Ca}}$); (b) Simulated solution with Ca^{2+} ($\text{C}_{+\text{Ca}}$); (c) Unfiltered supernatant (S_{raw}); (d) Filtrate after 0.45 μm microfiltration (S_{MF}); (e) Filtration by membranes with MwC of 10 kDa ($\text{S}_{10\text{k}}$); (f) Filtration by membranes with MwC of 1 kDa ($\text{S}_{1\text{k}}$).

size and morphology (Ronteltap et al., 2010). Particles of sizes $> 0.45 \mu\text{m}$ in the S_{RAW} solution might have served as seed material. However, although crystals of regular morphology formed from the S_{RAW} solution, the ratio of N:Mg:P in the crystals was 18.74:3.84:1. This indicated that the crystals from the S_{RAW} solution contained a large amount of organic matter, from the perspective of component analysis through SEM-EDS elemental analysis (Fig. S5). The N:P ratios of S_{10k} and S_{1k} were 0.95 and 1.06, indicating that the phosphate was mainly struvite. The Ca:Mg ratios, which indicate the amounts of calcium salts, were 1.64 (S_{MF}), 0.92 (S_{10k}), and 1.21 (S_{1k}). The C:P ratios, representing the ratio of carbonate and phosphate, were 3.63 (S_{MF}), 1.63 (S_{10k}), and 1.35 (S_{1k}); since the initial concentrations of Ca and Mg were same, this implies that the absence of large MWt substance facilitates the precipitation of calcium carbonate. These results were determined by energy spectrum analysis of the crystal products. In the literature, needle-like, coffin-like, and trapezoidal shapes have been described as typical for struvite crystals. Morphologies that were X-shaped or dendritic were also reported as atypical (Ronteltap et al., 2010). Particle sizes $> 0.45 \mu\text{m}$ in the S_{RAW} solution have the potential to function as seed material.

Struvite crystal formation was inhibited due to the high concentration of high-MWt ($> 10 \text{ kDa}$) organic matter. It has been reported that organic ligands and macromolecular organic matter have inhibitory effects on the phosphate crystallization process (Van der Houwen and Valsami-Jones, 2001). Soluble organics from wastewaters may have formed complexes with ionic struvite reactants, thus making them less available for SAP. Mg^{2+} ions have been reported to react with soluble organic matter (Karabegovic et al., 2013). The large molecule binding effect on Mg was also observed (Fig. 4d). In addition, the co-precipitation of soluble organic compounds in struvite recovery reduces the purity of struvite (Liu et al., 2013). By contrast, the overall performance of organic matters with low molecule weight facilitated struvite crystallization, compared with the test without inoculation by organic matter ($C_{+\text{Ca}}$). The mechanism by which organic matter affects struvite crystallization remains unclear. For low molecular weight organic matters (citric acid, succinic acid and acetic acid) (Song et al., 2014), the smaller molecular size results in weaker adsorption and less pronounced effects on the active sites of crystal nuclei. Moreover, it displays less inhibitory effect on the MAP crystallization process. A possible explanation is that organic matter could bind to ions, thereby affecting ionic activity (Ronteltap et al., 2010; Udert et al., 2003). It was found that increasing the calcium concentration reduces crystal size and inhibits struvite growth, or affects struvite crystallization and leads to the formation of an amorphous substance rather than crystalline struvite (Le Corre et al., 2005). Lower MWt matters undergo complexation with calcium, and inhibit the competitive effect with Mg^{2+} toward PO_4^{3-} . This phenomenon was related to the functional group content and molecular size of the organic acids. Matsumoto and Funaba (2008) found that organic matter with MWt $< 8 \text{ kDa}$ acted as a trigger for crystallization of struvite in cat urine.

These results suggest that phosphorous recovery should be placed downstream of anaerobic fermentation and coupled with sludge pretreatment. This arrangement should not only

improve the release of ammonia and phosphate, but should also reduce the interfering effects organic matter of high MWt. The levels of solids, inorganics and organics in the pretreated sludge influenced SAP, which suggests that case-by-case testing and process optimization are required to improve the applicability of phosphorus recovery. These findings emphasize the need for further research into appropriate types of organic matter and the cut-off effect.

3. Conclusions

- (1) Selective release of carbon, nitrogen, phosphorus, Ca^{2+} , and Mg^{2+} can be achieved by sludge pretreatment using MW-hybrid processes. MW- H_2O_2 is the recommended sludge pretreatment process for phosphorus recovery in the form of struvite. The ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{N}:\text{PO}_4^{3-}-\text{P}$ was 1.2:2.9:1 in the supernatant.
- (2) Pre-treatment conditions strongly affect the MWtD of the soluble matter released, mainly polysaccharides and protein, as a consequence of hydrolysis and the oxidative effect of pretreatment.
- (3) Low COD facilitates the removal of NH_4^+-N and $\text{PO}_4^{3-}-\text{P}$ via crystallization, and the amorphous struvite crystals ($< 1 \text{ kDa}$) obtained from the filtered solutions have high purity. Therefore, the present study reveals the necessity of taking into consideration the interfering effect of high MWt organic matter during struvite crystallization from sewage sludge.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.10.008>.

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