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Selective release of phosphorus from waste-activated sludge by low-temperature thermal treatment: comparative study with ultrasonic treatment

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ABSTRACT

Phosphorus (P) is a limited and irreplaceable resource and its recovery has become critical for sustainable society. Waste-activated sludge (WAS) is an important source for P recovery. For selective release of P, thermal treatment at low temperature (50–80˚C) was applied to WAS and the release characteristics of P, nitrogen (N), and organic compounds were investigated. Thermal treatment showed that P release is positively associated with temperature and treatment time. Thermal treatment of sludge at 50–80˚C released 25–32% of total P (T-P) in 2 h. Inorganic phosphate (Pi) release was 19–22% of the T-P in the sludge, while polyphosphate (poly-P) release was 2–9% of the T-P at 50–80˚C. Pi was the dominant P compound (85% of the released T-P) in the supernatant at 50˚C and its proportion decreased to 56% at 80˚C, while the proportion of poly-P in the supernatant increased at higher temperature. During the initial 30 min of thermal treatment at 50˚C, the amount of released N exceeded that of P at 80˚C. However, P was the major compound released after 2 h, followed by N and organic compounds. On the other hand, ultrasonic treatment of WAS showed no preferential release of specific compound and proved the selective release of P with low-temperature thermal treatment.

Keywords: Low-temperature thermal treatment; Phosphorus recovery; Selective phosphorus release; Ultrasonic treatment; Waste-activated sludge

1. Introduction

Phosphorus (P) is an indispensable element for the synthesis of ribonucleic acids (DNA and RNA) and phospholipids. All the living organisms cannot survive without P, because it cannot be replaced by any other element. P is produced by neutralization of phosphoric acid from phosphate rock to produce P fertilizers and other chemicals. Considering current P consumption rate, terrestrial phosphate reservoir is estimated to be exhausted in about 100 years [1]. Therefore, P recycling becomes a critical task for the world. Most of the used P flows into wastewater and is accumulated in waste sludge during wastewater treatment, therefore P recovery from wastewater and waste sludge has recently attracted a lot of attention.

Wastewater treatment with activated-sludge process can produce sludge with P content in the 2 and

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3% range on a dry-weight basis. Enhanced biological P removal process, which is designed to culture communities of P accumulating organisms (PAO) has the ability to store intracellular P in the 6–8% range on a dry-weight basis [2]. P is used for the biosynthesis of ribonucleic acids, phospholipids, and phosphate, including nucleoside phosphate (ATP, ADP, and AMP) in waste-activated sludge (WAS). Apart from these molecules, PAO contain a significant amount of polyphosphates (poly-P), in which the excessive inorganic phosphate (Pi) is stored [3]. Poly-P is also used as a raw material in the food processing and pharmaceutical industry [4].

Even though WAS contains high amounts of P, it cannot be directly applied to agricultural land, because it is usually contaminated with pathogens, heavy metals, or other pollutants [5]. One of the most effective methods of P recycling is to remove P from wastewater and capture it with crystallization as hydroxyapatite ($Ca_5(PO_4)_3OH$) or struvite ($MgNH_4PO_4$) by adding cations such as Ca^{2+}, Mg^{2+}, and NH_4^+ [6].

Intensive research has been conducted on the recovery of P from sludge and sludge ash. P can be released from sludge either with sludge hydrolysis or with selective excretion through cell membranes or walls. Sludge hydrolysis or solubilization is the release of cellular organelles into a liquid by breaking down cellular membranes or walls [7,8]. Selective excretion occurs when intracellular materials are excreted through cell membranes or walls, while maintaining their cellular structure. Sludge hydrolysis or solubilization can be succeeded with mechanical, chemical, and thermal treatment at 120–200˚C [7–9], and P compounds are released along with the cellular organelles. Thermal sludge treatment (120–200˚C) has been effective in sludge hydrolysis, but it has some drawbacks due to higher energy cost and lack of P selectivity in the release. Although extensive research has been conducted on the release or solubilization of organic components with sludge pre-treatment [10–12], information on P release with thermal treatment at low or moderate temperatures is limited. Microorganisms release P with heat shock, a method that is relatively economic, because a low amount of chemicals and energy is required for sludge treatment.

Most recent studies on sludge treatment have focused on the solubilization of organic compounds, as a pre-treatment method that enhances anaerobic digestion, while only a few of them have examined P release from sludge [12–15]. Kuroda et al. [12] and Takiguchi et al. [13] reported the release characteristics of P with thermal treatment at low temperature (50–90˚C) from laboratory-grown PAO. Tao and Xia [14] investigated the release characteristics of P, nitrogen (N), organic compounds, and some metal cations during the thermal treatment of excess sludge. Wang et al. [15] demonstrated that the release rate and the amount of chemical oxygen demand (COD), total N (T-N), and total P (T-P) during ultrasonic sludge treatment were not significantly different above critical ultrasonic irradiation intensity. Also, Kim and Yoon [11] compared the effectiveness of ultrasonic treatment and thermal treatment at low temperature for sludge hydrolysis and organic solubilization.

In this study, we investigated the selective release of P over other components (N and organic compounds that measured as COD) from WAS with low-temperature (50–80˚C) thermal treatment. Characteristics of P, N, and organic compounds released with thermal treatment were compared with those released with ultrasonic treatment, which is the mechanical disintegration of sludge. Pi, poly-P, and T-P were measured for analyzing P compounds released from WAS. The objectives of this study were (1) to determine the effect of temperature on the amount and forms of released P and (2) to identify the most effective treatment condition for the selective release of P and N.

2. Materials and methods

WAS was taken from the aeration basin of a municipal wastewater treatment plant in Chuncheon, Korea, which uses biological nutrient removal. It was then packed in an ice-box and transported to the laboratory, where it was placed in a 2-L cylinder for 30 min. The characteristics of WAS were as follows: pH 6.8, sludge volume index 135, 183 mg L^{-1} T-P, 553 mg L^{-1} T-N, 6,131 mg L^{-1} COD, 6,970 mg L^{-1} mixed liquor suspended solids (MLSS), and 0.695 mixed liquor volatile suspended solids/MLSS ratio.

Settled sludge was placed into 50-mL glass tubes, which were incubated at 50, 60, 70, and 80˚C in a temperature-controlled shaking water-bath (WSB-45, Daihan Scientific, Korea) for 10 min to 2 h. Then, 2-mL samples were centrifuged at 6,000× g for 10 min (Mega 17R, Hanil Science Industry, Korea) and filtered using GF/C™ glass fiber filters (Whatman, USA) for chemical analysis to determine Pi, poly-P, T-P, T-N, and COD in the supernatant. For the ultrasonic treatment, 0.5-L settled sludge was treated in 1-L beakers for 10 min to 1 h using an ultrasonic generator (TUB120710-064, Durasonic, USA) with an operating frequency of 28 kHz and a maximum input power of 233 W. Then, 2-mL samples were taken for chemical analysis in which: Pi was determined with the ascorbic acid method [16]; T-P was assessed as Pi after digestion of the sample with ammonium persulfate at 121˚C for 30 min; poly-P was measured after hydrolyzing the supernatant in 1 N H_2SO_4

at 95˚C for 15 min [17] and calculated by subtracting Pi amount in the supernatant before acid hydrolysis from that measured after acid hydrolysis; COD and T-N was analyzed according to the Standard Methods as described in APHA [16]. All sludge treatments and chemical measurements were repeated three times and the average values were used for analysis.

3. Results and discussions

The kinetics of P release from WAS during the thermal treatment. T-P, Pi, and poly-P were analyzed in order to investigate P release from sludge (Fig. 1). All P compounds released from sludge were expressed as a percentage (%) of T-P in sludge. Release of T-P and Pi was mostly active during the initial 10 min of the treatment and the release rates gradually decreased afterwards. Thermal treatment at 50–80˚C released 25–32% of T-P in 2 h, and the amount of T-P increased with treatment temperature. At 50˚C, T-P release became saturated after 1 h, but T-P was consistently increasing at higher temperature. About 19–22% of T-P was released as Pi. The amount of Pi remained constant at 50–80˚C, while T-P increased. Therefore, the difference between the amount of T-P and that of Pi was positively associated with temperature, which means that the release of P components, other than Pi increased at higher temperatures. Kulaev and Vagabov [18] showed that Pi was taken up and released by Pi transport system, which was continuously expressed *in vivo* condition. However, the enzymatic transport system was probably not functional at the experimental temperature range (50–80˚C) used in this study. On the other hand, release of poly-P increased from 2% (50˚C) to 9% (80˚C) of T-P at the same temperature. In addition, saturation time of poly-P release was shorter at higher temperature, and poly-P release was completed in 30 min at 80˚C. Data analysis of P (T-P, Pi, poly-P) release showed that different P compounds with different permeability to cell membranes or walls, were released from sludge during the thermal treatment (Fig. 1). If sludge contained only a single P compound, then P release kinetics would follow first-order kinetics. As shown previously (Fig. 1), data obtained from this study did not follow first-order kinetics, which was also observed using graphical data analysis (data not shown). The proportion of Pi in T-P decreased with thermal treatment time, while the proportion of higher molecular weight P compounds increased. Pi is a low molecular weight P compound and consequently it has higher permeability than high molecular weight P compounds. As a result, Pi was released relatively earlier during the thermal treatment, while high molecular weight P compounds were released later during the treatment.

Thermal treatment temperature had a similar effect on P release characteristics with that of thermal treatment time (Fig. 2). The results of this study showed that about 85% of T-P was Pi at 50˚C and this percentage decreased to 50% at 80˚C. On the other hand, poly-P release and the proportion of poly-P in T-P

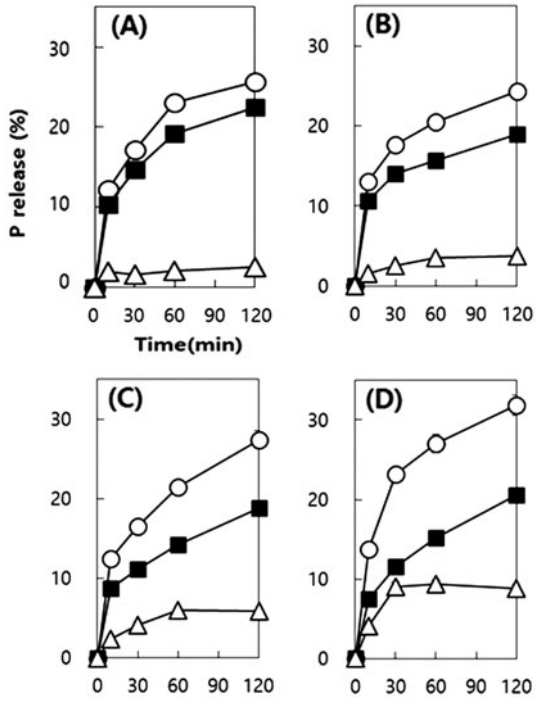

Fig. 1. Kinetics of phosphorus release from waste activated sludge with thermal treatment at (A) 50˚C, (B) 60˚C, (C) 70˚C, and (D) 80˚C. Graphs show the average concentration ratio of total phosphorus (○), inorganic phosphate (■), and polyphosphate (△) to total phosphorus in the supernatant.

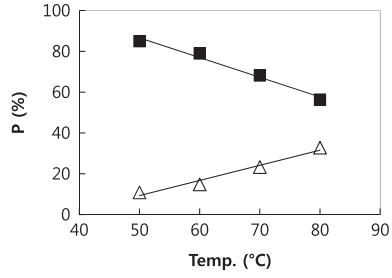

Fig. 2. Effect of sludge treatment temperature on the distribution of released phosphorus compounds in the supernatant. Graphs show the P ratio (%) of inorganic phosphate (■) and polyphosphate (△) to total phosphorus in the supernatant.

increased with temperature; however, it was shown that more than 50% of released T-P was Pi (Fig. 2), a percentage that was similar to that released with ultrasonic treatment. Wang et al. [15] reported that N removing sludge and also N and P removing sludge released 40 and 80% of T-P as Pi, respectively during the ultrasonic treatment, and also that more Pi was released from higher P containing sludge or PAO containing sludge.

It is known that poly-P is synthesized by polyphosphokinase and degraded by exopolyphosphatase, but the enzymes were probably not functional at the experimental temperature range (50–80˚C) used in this study. Sodium metaphosphate and pentasodium triphosphate were used as a model poly-P to test the possibility of poly-P degradation during the thermal treatment at the temperature range of 50–80˚C (Fig. 3). The results showed that Pi formation by poly-P hydrolysis was negligible at the temperature range of 50–80˚C. Furthermore, poly-P treatment with 1 N H_2SO_4 at 95˚C yielded more than 90% hydrolysis in 2 h, but poly-P was resistant to thermal hydrolysis at the temperature range of 50–80˚C. Ultrasonic poly-P degradation was also performed for 2 h, but it only yielded Pi that was less than 2% of T-P (data not shown). It is likely that Pi found in the supernatant was released during the thermal treatment and not due to extracellular hydrolysis of poly-P. Increased release of poly-P at higher temperature (80˚C) was probably caused by increased fluidity and permeability of cell membranes and walls [19].

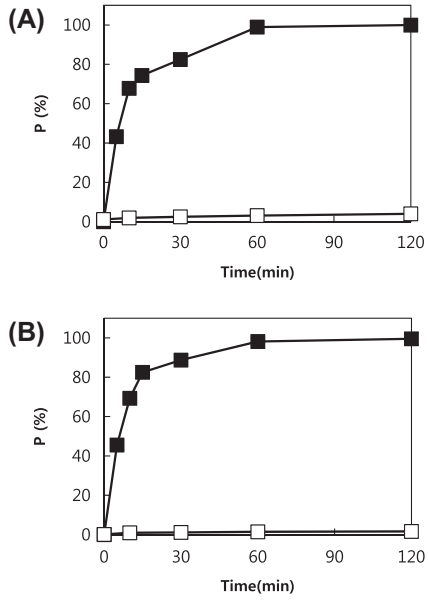

Fig. 3. Degradation of (A) sodium metahexaphosphate and (B) pentasodium triphosphate into inorganic phosphate with thermal (80˚C, □) and combined acid and thermal (1 N H_2SO_4 at 95˚C, ■) treatments.

Kuroda et al. [12] reported that T-P and Pi release increased at higher temperature during the thermal treatment. Specifically, T-P release was completed in 10–20 min at temperature higher than or equal to 80˚C, while T-P release continued for 2 h at lower temperature (50–60˚C). These differences could be explained mainly from the different content of poly-P and T-P in sludge that used in the experiment. Kuroda et al. [12] used laboratory grown PAO whereas WAS from a municipal wastewater treatment plant was used in this study. T-P and poly-P contents of PAO were 4.3 and 3.3%, respectively, on a dry-weight basis, that were higher than those of WAS (2.6% T-P and less than 1% poly-P) of this study.

T-N and COD in the supernatant during the thermal treatment were also measured for investigating the release characteristics of N and organic compounds. The kinetics of T-N and COD in the supernatant based on the percentage of T-N and COD in sludge before the treatment were investigated (Fig. 4). T-N and COD showed a similar trend with P and

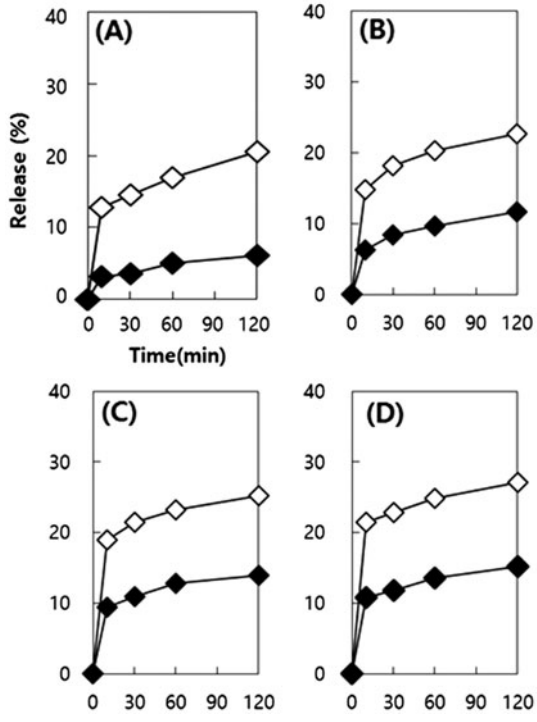

Fig. 4. Kinetics of total nitrogen (T-N) and chemical oxygen demand (COD) release from waste activated sludge with thermal treatment at (A) 50˚C, (B) 60˚C, (C) 70˚C, and (D) 80˚C. Graphs show the average concentration ratio of T-N (◇) and COD (◆) in the supernatant, based on T-N and COD in waste activated sludge, respectively.

increased with treatment temperature and time. T-N and COD release was mostly active during the initial 10 min of the treatment and the release rates gradually decreased afterwards. T-N release was in the 20.6–27.1% range, while COD release was in the 6.1–15.2% range at 50–80˚C after 2 h. During the treatment, T-N release was consistently higher than that of COD, probably because N compounds (mostly proteins) are generally excreted faster than organic compounds during the thermal treatment. These results were different than those obtained from ultrasonic treatment [11,15,20]. Kim and Yoon [11] and Wang et al. [20] showed higher release of COD than T-N, while Wang et al. [15] obtained similar release of COD and T-N. We assume that applied ultrasonic intensity may alter the release rate of compounds from sludge.

The release ratio of T-N and COD to T-P and allows the comparison of release characteristics of P, N, and organic compounds were investigated during the thermal treatment (Fig. 5). At 50˚C, both ratios were maintained consistently far below 1 throughout the thermal treatment; more specifically COD to T-P ratio was less than 0.3, while T-N to T-P ratio was about 0.8. At 60˚C, T-N release was about 10% higher than that of T-P for the initial 10 min, and it gradually decreased to 90% of T-P release. COD to T-P ratio was slightly higher than 0.4. Initial ratio of T-N to T-P increased sharply with temperature. At 70˚C, the ratio of T-N to T-P was about 1.5 during the initial 10 min, and gradually decreased afterwards, while the ratio of COD to T-P was about 0.4 after 2 h. At 80˚C, the ratio of T-N to T-P was about 1.6 during the initial 10 min and gradually decreased to 0.8 in 2 h, while the ratio of COD to T-P was in the 0.4–0.5 range after 2 h. Wang et al. [15] showed that the ratio of COD and T-N to T-P was about 1 during ultrasonic treatment (0.5 W mL^{-1} for 1 h) of WAS. They also reported that N and P removing sludge released more T-P, T-N, and organic compounds than N removing sludge during ultrasonic treatment.

It was reported that during thermal-alkaline treatment, solubilization of WAS started with carbohydrates followed by proteins, and then by fats and lipids [8]. However, WAS disintegration with ultrasound treatment showed that fats and lipids were solubilized first, followed by proteins and amino acids,

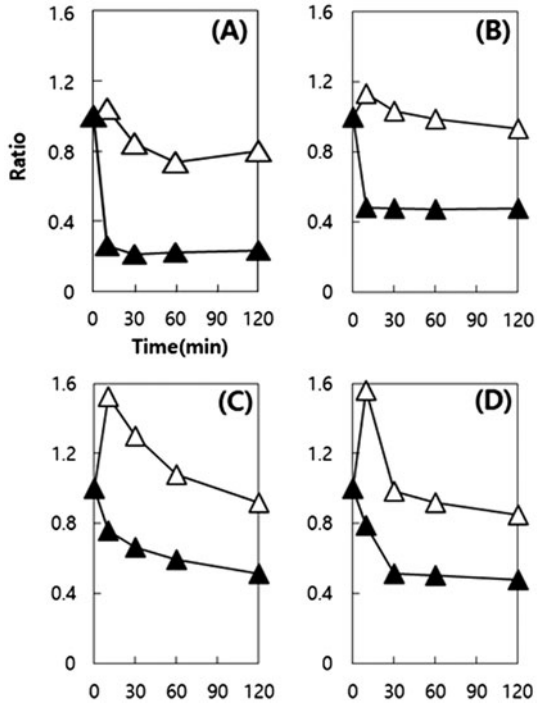

Fig. 5. Kinetics of the ratio of total nitrogen (△) and chemical oxygen demand (▲) release to total phosphorus release from waste activated sludge with thermal treatment at (A) 50˚C, (B) 60˚C, (C) 70˚C, and (D) 80˚C.

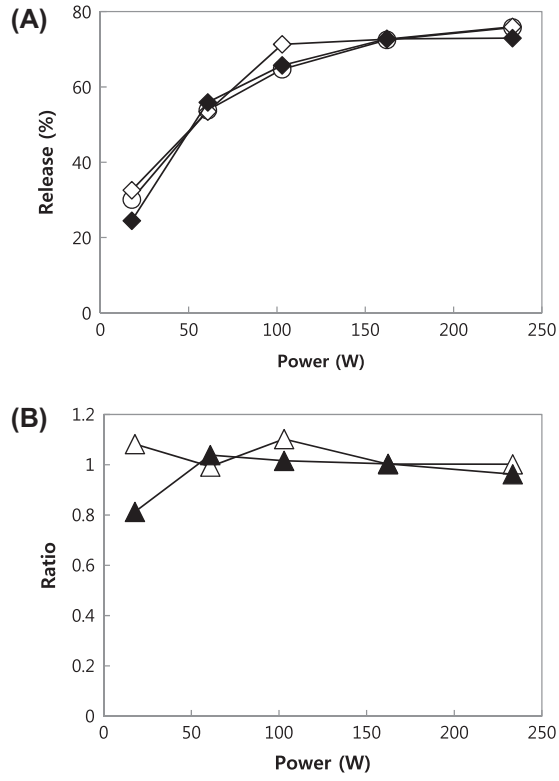

Fig. 6. Release of total phosphorus (T-P: ○), total nitrogen (T-N: ◇), and chemical oxygen demand (COD: ◆) from waste activated sludge after ultrasonic treatment for 1 h at different power (A) and the ratios of T-N and COD to T-P after the ultrasonic treatment (B). (T-N/T-P: △; COD/T-P: ▲).

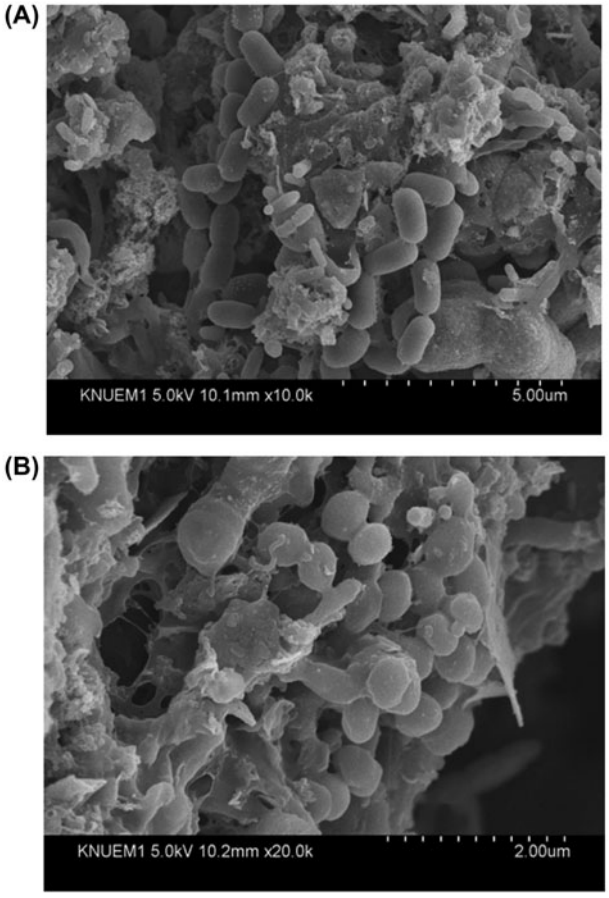

Fig. 7. Waste activated sludge samples before (A) and after (B) the thermal treatment at 80˚C for 2 h. All samples were fixed in glutaraldehyde and osmium and observed by scanning electron microscope.

and then by carbohydrates [11]. These difference might be due to the different treatment methods that used and also because alkaline treatment denatures proteins [8].

The release of P, N, and COD [A] and their release ratios [B] from WAS after 1 h ultrasonic treatment were investigated (Fig. 6). The release of T-P, T-N, and COD increased with the ultrasonic power and saturated above 160 W. Different to the thermal treatment, ultrasonic treatment of WAS showed similar release characteristics of T-P, T-N, and COD release (Fig. 6(A)). The release ratios of T-N and COD to T-P both were close to 1 when the ultrasonic power higher than 160 W was applied (Fig. 6(B)). The result indicates that ultrasonic treatment does not give any selective release of specific compound from WAS, and the compounds were released by hydrolysis or mechanical disintegration of WAS. On the other hand, thermal treatment (50–80˚C) for 2 h released T-P first, followed by T-N, and then by COD. These results indicated that the release by thermal treatment was not exclusively due to the break down or complete hydrolysis of sludge. Additionally, electron microscopic observation revealed that sludge maintained its structure after thermal treatment (Fig. 7).

Thermal treatment at higher temperature for longer time was shown to be the most effective strategy for P release and recovery, when energy cost is not a concern. Selective release of P over N and organic compounds was more effective when lower temperature (50˚C) and longer treatment time were used. It is known that WAS usually undergoes anaerobic digestion for stabilization after thermal treatment for P release and recovery. The enhancement of anaerobic digestion after thermal treatment was tested by Ferrer et al. [10] and revealed that biogas production increased up to 30% after pre-treatment at 70˚C. Simultaneous release and recovery of P and N compounds as struvite might also be an effective method for anaerobic digestion of residual sludge, because ammonia inhibition could be reduced or even eliminated.

4. Conclusions

Thermal treatment at 50–80˚C for 2 h showed that P release was positively associated with the temperature and time. Pi release was 19–22% of T-P, while poly-P release was 2–9% of T-P at 50–80˚C. Pi was the dominant P compound (85% of T-P) in the supernatant at 50˚C and its proportion decreased to 56% at 80˚C, while poly-P was the dominant P compound in the supernatant at 80˚C and its proportion decreased at 50˚C. During the thermal treatment, N compound was actively released in the initial 30 min of treatment at 80˚C. However, P was the major compound released after 2 h, followed by N and organic compounds. This study showed that thermal treatment at 50–80˚C promotes selective release of P and N and not the release of cellular compounds due to hydrolysis.

Acknowledgments

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