Accelerated anaerobic release of K, Mg and P from surplus activated sludge for element recovery and struvite formation inhibition

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ABSTRACT

Accelerated release of potassium (K), magnesium (Mg) and phosphorus (P) from surplus activated sludge (SAS) was investigated to develop a new system for the recovery of the elements. Anaerobic cultivation of SAS during 24 h released 78% of K and about 50% of Mg and P from SAS more effectively compared to aerobic cultivation (K: 40%, Mg: 15%, P: 15%). Furthermore, the addition of sodium acetate as an organic carbon source remarkably accelerated the release of K, Mg and P from SAS under anaerobic condition. However, no increase in the maximum release efficiencies was observed. The elements released from SAS could be transferred to separate liquid with the existing mechanical thickener and be recovered as MgKPO₄ by some additional process. Furthermore, the removal of the elements from SAS would inhibit the formation of struvite causing the blockage of sludge transport pipe after anaerobic digestion process of thickened sludge.

Key words | anaerobic release of elements, element recovery, inhibition of struvite formation, surplus activated sludge

INTRODUCTION

Almost all of phosphorus (P) and potassium (K) used in Japan have been imported mainly as minerals from other countries. These elements are recognized as non-renewable ones. About 10% of the imported phosphorus is entered to sewage treatment plants and then most of P in sewage is transferred to primary and secondary sludges (Japan Ministry of Land Infrastructure transport and tourism 2010). On the other hand, anaerobic digestion process of secondary sludge with raw sludge is very attractive in terms of energy recovery. However, this process causes the release of phosphate (PO₄³⁻) and cations (Mg²⁺, K⁺, NH₄⁺) from secondary sludge and the subsequent formation of phosphate salts such as struvite (MgNH₄PO₄·6H₂O) resulting in the blockage of sludge transport pipes by their scaling (Doyle & Parsons 2002).

Choi et al. (2011) and Wang et al. (2014) have confirmed that K and Mg concentrated probably as polyphosphate compound in activated sludge microorganisms through anaerobic and aerobic cycles are released together with P from the activated sludge under anaerobic condition. This finding suggests that K, Mg and P could be removed from surplus activated sludge (SAS) to liquid phase under anaerobic condition. For their removal, two additional processes are required: a cultivation tank for the elements release from SAS and the subsequent separator for liquid and solid phases. However, if the elements’ release can be accelerated and enhanced, the existing SAS transport pipe from secondary clarifier and mechanical thickener could be respectively used as an anaerobic reactor for the elements release and as a liquid and solid separator for the elements’ removal from SAS.

The purposes of this study were to investigate (1) the behaviour of the elements in the SAS from secondary clarifier to mechanical thickener, (2) the effects of organic carbon source addition and temperature on acceleration of anaerobic K, Mg and P release from SAS using a batch reactor and (3) the usability of primary effluent and dewatered separate
liquid of digested sludge as an alternative organic carbon source.

MATERIALS AND METHODS

In this study, the five different samples were taken at a sewage treatment plant in Iwate Prefecture, Japan as shown in Figure 1. In this plant, sewage is treated by a conventional activated sludge process including partial anaerobic zone at the front of aeration tank. The SAS is concentrated with a mechanical thickener and then the thickened SAS is mixed with thickened raw sludge. The mixed sludge undergoes a mesophobically anaerobic digestion process. The blockage of the screen in a screw press dewatering machine after anaerobic digestion process has occurred in this plant. The primary effluent and return activated sludge (RAS) used in this study were taken from two different inlets of aeration tank, respectively. The SAS was taken from the sludge transport pipe immediately before mechanical thickening process. Two different types of separate liquid were taken from a centrifugal thickener for SAS and a screw press dewatering machine for digested sludge, respectively. As described below, the samples were pretreated to separate liquid and solid phases as soon as possible after arrival at the laboratory on the sampling day.

The pH of the sludge samples was measured with a pH meter (HM-25R, TOA DKK, Japan). The total and volatile solids (TS and VS) were analyzed by drying the sludge sample at 105°C and the subsequent ignition of dried sample at 550°C. The sludge and separate liquid samples were centrifuged at 10,000 rpm for 10 min and then the supernatants were filtrated using a membrane filter with a pore size of 0.45 μm to measure the dissolved components. The concentration of dissolved organic carbon (DOC) was determined with a total organic carbon (TOC) analyzer (TOC-VCSH/CSN, Shimadzu, Japan). Ammonium nitrogen in the filtrate was measured using a UV/VIS spectrometer (Auto Analyzer, BL TEC KK, Japan) by the phenate method. The non-filtered and filtered samples of the sludge and separate liquid were digested with heated nitric and hydrochloric acids. The digested samples were filtered using the same filter as mentioned above. The concentrations of Al, Ca, Fe, K, Mg and P in the filtrate were analyzed with an inductively coupled plasma optical emission spectrometer (ICP/OES, ICPE-9000, Shimadzu, Japan). The analyses were conducted on the basis of Testing Methods for Sewage (Japan Sewage Works Association 2012).

For a batch cultivation experiment, the fresh RAS samples were taken into 1-L opened shaking flasks and 50-mL capped test tubes. Sodium acetate (SA, carbon content: 0.29 mg C/mg CH₃COONa) solution was prepared as an organic carbon source for activated sludge microorganisms and was added to the RAS samples to evaluate whether the element release is enhanced or not. The SA concentrations were adjusted to 50, 100, and 500 mg/L, respectively. The control sample with no addition was also prepared. Oxygen gas in the sample of the test tubes was reduced with N₂ gas for anaerobic cultivation. The samples were cultivated with shakers at 25°C and 35°C for 24 h. The samples collected from the flasks and tubes were centrifuged at 10,000 rpm for 10 min and the supernatants were filtrated with a membrane filter to analyze dissolved elements. As described previously, the filtrates were preliminarily treated and the element concentrations were measured. The DOC of the filtrates was measured with the TOC analyzer to understand the microbial uptake of acetate. TOC in the diluted SA solutions was also measured to obtain the initial concentration of DOC which was expressed as the summation of the DOC concentrations of the sludge sample and the diluted SA solutions. Ammonium nitrogen was...
measured to examine the degree of anaerobic degradation of sludge sample. Table 1 shows the general property and the concentration of the major elements in the RAS used in the batch cultivation experiment.

**RESULTS AND DISCUSSION**

**Behaviour of the elements in SAS**

Table 2 shows the total and dissolved concentrations of elements and their ratios in the RAS, the SAS before the centrifugal thickening and the separate liquid from the centrifugal thickener. The samples were collected twice on two different dates and the averages of the data obtained are provided. There was no large difference of the values between the sampling dates. The total concentrations of Mg, P, K, Ca, Al and Fe in the SAS were 57.2 mg/L, 217 mg/L, 62.8 mg/L, 48.9 mg/L, 12.8 mg/L and 17.0 mg/L, respectively. The ratios of dissolved to total concentration of Mg and P were about 0.1 in RAS (DR/TR) and SAS (DS/TS). This result suggested that Mg and P were insignificantly released from SAS while being transported through sludge transport pipe from the bottom of the secondary clarifier to the mechanical thickener. Furthermore, the total concentration ratios of separate liquid to SAS (TSL/TS) of Mg and P were around 0.15, indicating that Mg and P were slightly transferred from SAS to separate liquid after mechanical thickening. Therefore, it will be necessary to accelerate the release of the elements from the SAS in order to transfer more elements to the separate liquid.

**Accelerated release of elements from SAS**

In order to find out the better conditions to accelerate the release of the elements from SAS, the effects of organic carbon source addition and temperature were investigated through the batch experiments for cultivation of the SAS. In this batch experiment, the RAS was used as an alternative of the SAS immediately after being discharged from the bottom of the secondary clarifier because the corresponding SAS could not be sampled.

Figure 2 shows the variations in the pH and the concentrations of NH₄-N and DOC in the RAS under aerobic and anaerobic conditions at 25 °C (Experiment No. 1). The pH values were decreased from 6.8 to around 5.7 except for the SA concentration of 500 mg/L under aerobic conditions. Anaerobic conditions showed no significant variations in the pH values. It has been reported that the pH of minimum struvite solubility ranges from 8.0 to 10.7 (Doyle & Parsons 2002). Therefore, struvite would not be formed during this short-term cultivation. The concentrations of NH₄-N were decreased from 18 mg/L to less than 6 mg/L under aerobic conditions, which implies that nitrification occurred and

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>pH</th>
<th>TS g/L</th>
<th>VS mg/L</th>
<th>Al mg/L</th>
<th>Ca mg/L</th>
<th>Fe mg/L</th>
<th>K mg/L</th>
<th>Mg mg/L</th>
<th>P mg/L</th>
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<tbody>
<tr>
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<td>7.1</td>
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</tr>
<tr>
<td>2</td>
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<td>13.7</td>
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<td>63.5</td>
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<table>
<thead>
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<th>Elements</th>
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<th>SAS</th>
<th>Separate liquid</th>
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<tr>
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<td>Tₛ</td>
<td>Dₛ</td>
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<tr>
<td>Mg</td>
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<td>6.55</td>
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<tr>
<td>Fe</td>
<td>18.6</td>
<td>0.36</td>
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Tₛ and Dₛ: total and dissolved concentrations (mg/L). i: sample type. NA: not available.
resulted in the decrease in the sludge pH. Under anaerobic conditions, NH₄-N was gradually increased except for no SA addition (0 mg/L). This indicates that anaerobic degradation of activated sludge microorganisms was slight during the cultivated period of 24 h. The DOC concentrations were rapidly decreased during the first 1 h under both aerobic and anaerobic conditions where SA was added. These decreases are due to the uptake of acetate by activated sludge microorganisms. When the ratio of SA (500 mg/L) to VS (7.1 g/L) was about 70 mg SA/g VS (21 mg DOC/g VS) under anaerobic condition, acetate was incompletely consumed. This result suggests that the microbial uptake of acetate was sufficiently conducted by coexistent facultative anaerobic microorganisms such as phosphorus accumulating organisms (PAOs).

Figure 3 shows the variations in the release efficiencies of Mg, P, K and Ca from the RAS under aerobic and anaerobic conditions at 25 °C (Experiment No. 1). The release efficiency was calculated by dividing the dissolved element concentration at a certain time by the total one shown in Table 1. The anaerobic conditions showed higher release efficiencies of K, Mg and P compared to aerobic conditions. The initial release of Mg, P and K was accelerated under anaerobic conditions since the uptake of acetate was increased with an increased DOC concentration as shown in Figure 2. The maximum release efficiencies were 78% for K and about 50% for Mg and P (Table 3). These results suggest that the anaerobic release of Mg, P and K from the SAS could be achieved during a short term of about 6 h in the sufficient presence of DOC source such as SA. However, higher concentrations of DOC added showed no enhancement of maximum release efficiencies of Mg and P (Figure 3 and Table 3).

On the other hand, Ca was gradually released except for the SA concentration of 500 mg/L under aerobic conditions and the maximum efficiency was about 35%. The addition of SA under anaerobic conditions accelerated the initial release of Ca from SAS, although the maximum efficiency was less than 30%, which was lower compared to those of Mg, P and K. The enhanced Ca release under aerobic conditions would be owing to the decrease in the sludge pH as shown in Figure 2. The release efficiencies of Al and Fe were less than 5% during 24 h, respectively.

In the sewage treatment plant investigated in this study, the activated sludge undergoes anaerobic and aerobic cycles in the aeration tank. This suggests that phosphorus is accumulated as polyphosphate compounds in the cells of PAOs in the activated sludge, and K⁺ and Mg²⁺ are also stored as counter ions forming polyphosphate compounds (Schönborn et al. 2001; Choi et al. 2011). Under anaerobic condition, polyphosphate compounds are degraded into PO₄³⁻, Mg²⁺ and K⁺ to produce adenosine triphosphate as an energy
source for conversing volatile fatty acid to polyhydroxyalkanoate (Barat et al. 2005; Choi et al. 2011; Yuan et al. 2012). Therefore, anaerobic release of these elements as shown in Figure 3 would result from the degradation of polyphosphate compounds in PAOs in the RAS.

Figure 4 shows the variations in the NH₄-N and DOC concentrations in the RAS under anaerobic conditions at 25°C and 35°C (Experiment No. 2). The pH values of the RAS samples ranged from 6.2 to 7.1 during the experiment. Anaerobic condition at 35°C brought about higher concentration of DOC and NH₄-N compared to that at 25°C, which indicates that anaerobic degradation of the organic substances in the RAS was promoted by heating mildly up to 35°C.

Figure 5 shows the variations in the release efficiencies of Mg, P, K and Ca from the RAS under anaerobic conditions at 25°C and 35°C (Experiment No. 2). The releases of Mg, P and K at 35°C were accelerated with an
increased SA concentration. Such tendency was consistent with the results obtained from the similar investigation by Wang et al. (2016). The efficiencies during the first 1 h at 35 °C were higher than those at 25 °C. The maximum efficiencies showed 50% of Mg and P, 75% of K and 40% of Ca. No apparent improvement of maximum efficiencies was observed during 24 h except for Ca, even though the cultivation temperature was increased from 25 °C to 35 °C.

The release efficiencies of Al and Fe were less than 10% at all of the conditions. From the results obtained in this study, it was found that the optimum SA concentration and temperature for the accelerated release of Mg, K and P were 500 mg/L and 35 °C, respectively.

In the case of a sewage treatment plant investigated in this study, the retention time of the SAS in its transport pipe from secondary clarifier to mechanical thickeners is within 2 h and the treated amount of SAS per one thickener is about 20 m³/hr. In order to release the elements from the
SAS, the sludge retention time of at least 12 h would be needed as shown in Figures 3 and 5 where no organic carbon source is added to the SAS, which means that the additional tank with a volume of more than 200 m³ is required for cultivating the SAS at a retention time longer than 10 h per one thickener. However, if the sufficient organic carbon source and the heat are supplied to the SAS after being discharged from the bottom of secondary clarifier, the sludge retention time could be reduced to 2 h as shown in Figure 5, which suggests that the existing transport pipe could be utilized as an anaerobic cultivation reactor for the elements release from the SAS.

The present study has not revealed that a mechanical thickener can remove the released elements from SAS to separate liquid and as a result the struvite formation can be inhibited during the subsequent anaerobic digestion process. These projects need to be investigated in practical sewage treatment plant which has a chronic problem on the blockage of sludge transport pipe by struvite formation after anaerobic digestion process.

The dissolved concentrations of Mg, K and P released from the RAS were approximately 30 mg/L, 40 mg/L and 100 mg/L under anaerobic condition, respectively. In terms of the valuable elements recovery and recycling, it is desirable that these elements are finally recovered as MgKPO₄·6H₂O (Xu et al. 2015) from the separate liquid after mechanical thickening process. However, their recovery would be inefficient because Mg and K concentrations are low in the separate liquid. Therefore, further studies will be needed to develop a new process to concentrate the elements for the efficient recovery.

**Usability of primary effluent and dewatered separate liquid as organic carbon source**

Through the batch cultivation experiments described above, it was confirmed that the elements’ release from the SAS was accelerated by the addition of SA. In order to evaluate the potential usability of alternative organic carbon sources obtainable easily in sewage treatment plants, the DOC concentrations of the primary effluent and dewatered separate liquid were compared with that of the 500 mg/L SA solution (theoretical DOC: 145 mg/L). The DOC concentrations in the primary effluent and dewatered separate liquid were respectively 20.9 mg/L and 49.6 mg/L, which were lower than that of 500 mg/L SA solution. In such case, it is proposed that a part of thickened sludge is hydrolysed to short chain fatty acids to obtain an alternative organic carbon source with low alkalinity (e.g., Ucisik & Henze 2008; Xiong et al. 2012) and then is supplied to the SAS transport pipe as shown in Figure 6. Thickened raw sludge would be more suitable as an organic carbon source, because it could be more easily hydrolyzed than thickened SAS.

Our suggested process will additionally need the pipeline and pump for transferring thickened raw sludge to the SAS transport pipe and its power (Figure 6). However, this operation would not be so cumbersome. On the other hand, the washing of the pipe with detergents such as inorganic or organic acids is frequently conducted for cleaning the pipeline. This option is expensive and cannot prevent unexpected blockages of the pipe and screen in a dewatering machine. The suggested process could bring about less frequency of washing and solve the unexpected blockage.
CONCLUSIONS

In a sewage treatment plant investigated in this study, no release of the elements from the SAS occurred in the process of being transported from the bottom of secondary clarifier to mechanical thickener. The anaerobic cultivation of the SAS brought about the acceleration of Mg, P and K releases in the presence of SA as an organic carbon source. This finding suggests the possibility that the elements could be released from the SAS while passing through the existing transport pipe and be transferred to the separate liquid by the subsequent mechanical thickener. Reducing the releasable Mg content in thickened sludge would contribute to the inhibition of struvite formation causing the blockage of the sludge transport pipe after anaerobic digestion process.

REFERENCES


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