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# Optimization of phosphorus reduction in BNR process for urban watershed management

Yoon-Mi Choi<sup>a</sup>, Koo-Ho Kwon<sup>a</sup>, Si-Won Kim<sup>a</sup>, Seungyoon Lee<sup>b</sup>, Kyung-Sok Min<sup>a,\*</sup>

<sup>a</sup>Department of Environmental Engineering, Kyungpook National University, Daegu, 702-701, Korea Tel. +82 53 950 6581; Fax: +82 53 959 7734; email: ksmin@knu.ac.kr <sup>b</sup>K-water institute, Korea Water Resources Corporation, Daejeon, 305-730, Korea

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# ABSTRACT

The removal of the phosphorus contained in wastewater can be carried out by physic-chemical or by biological phosphorus removal (EBPR) process. Currently, the biological phosphorus removal process has been attracting attention. Because of its low capital and operational costs compared with those of chemical precipitation processes. According to the U.S. Environmental Protection Agency (EPA), TP<sub>off</sub> concentration decrease to 0.3 mg/l by using the biological treatment [1,2]. Therefore, in this study, we experimented with enhancing the BNR process by injecting an external carbon source into the anaerobic phase. Afterwards, when the phosphorus was released or accumulated in poly-p accumulating organisms (PAOs), we measured the behavior of cations. When the BNR process is injected with an external carbon source in the anaerobic phase was operated, the removal efficiency of TP in the effluent was 94.48% at the maximum, and Org-P, which is difficult to remove by chemical treatment only, was removed considerably. Likewise, some of the external carbon source affected the nitrogen removal. By estimating the metal cations concentration in the anaerobic phase, K<sup>+</sup>, Mg<sup>2+</sup> was used as a parameter to control the amount of external carbon which had to be injected. Our results showed that TP treatment with BNR met the criteria of effluent quality and is a cost-effective and environmentally sound alternative when compared with chemical treatment.

*Keywords:* Phosphorus removal; External carbon source; Behavior of cation; K<sup>+</sup>; Ca<sup>2+</sup>; Mg<sup>2+</sup>

## 1. Introduction

Currently, the South Korean government has issued an policy to secure high quality drinking water and river water for people has taken policy, "The Four Major River Restoration Project", "Total Maximum Daily Load (TMDL)". Also, permit limits of  $\mathrm{TP}_{_{\mathrm{eff.}}}$  concentration in South Korea will be 0.2 mg/l in 2012, about 90% less than previous year's permit limits.

To meet the strengthened wastewater quality standard that has been implemented since January 1, 2008, the advanced wastewater treatment system within wastewater treatment plant was introduced. However, TP<sub>eff</sub> at the advanced wastewater treatment system reached only 1.1 mg/L (TP<sub>eff.</sub> of a non-advanced waste-water treatment system TP<sub>eff.</sub> = 1.4 mg/L). This indicates well that the installed advanced wastewater treatment system has not been properly managed. Moreover, facilities are under construction to apply chemical precipitation to meet the wastewater quality standard to be

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<sup>\*</sup>Corresponding author.

implemented in 2012, which will incur a large amount of extra expenses for the chemical flocculate.

To minimize such maintenance expenses and utilize the introduced advanced wastewater treatment system more effectively, the biological treatment introduced in this study was applied to existing treatment facilities and more attention was paid to maintain concentration  $TP_{eff.}$  around 0.2 mg/l, which is required in the waste water quality standard in 2012.

However, the concentration of organic matter which affects nitrogen (N) and phosphorus (P) removing efficiency is not enough in domestic wastewater [3,4].

To supplement the insufficient organic substrate, the injection of an additional external carbon source can be an alternative, but it is very difficult to predict exactly the amount of injected external carbon source. That is, injecting an external carbon source such as CH<sub>3</sub>COOH, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> is so inevitable that it supplements the lack of Chemical Oxygen Demand (COD) in the domestic sewage.

Poly-p accumulating organisms (PAOs) store  $PO_4$ , which is a compounded of potassium and manganese ( $K_x Mg_y (PO_3)$ ). These metal cations are released and dissolved simultaneously with phosphorus in the anaerobic phase [5].

In other words, the dissolved cation concentrations are important parameters that can predict the orthophosphorus concentration in anaerobic phase.

Of course, this process requires energy and, an acetate can be good energy. Acetate is the biodegradable soluble Chemical Oxygen Demand (bsCOD) or readily biodegradable Chemical Oxygen Demand (rbCOD) fermented in the anaerobic phase, which PAOs can consume easily and rapidly during the anaerobic phase [6].

Based on these theories, if the cation concentration in the anaerobic phase is low, it should be increased by injecting an external carbon source. Likewise, if the cation concentration in anaerobic phase increases, it should be lowered by stopping the injection of an external carbon source.

During our research, we learned that organic phosphates, which were difficult to remove by chemical treatment, were removed by injecting an external carbon source. Currently, the chemical precipitation reactor and 2-stage filtration are being installed at the back (BNR+ chemical precipitation +2stages filteration), and more efforts are being put forth to reduce the concentration TP down to 0.05 mg/l. In the U.S., after the biological treatment,  $TP_{eff.}$  concentration decreased to 0.029 mg/l by using additional chemical precipitation reactor and 2-stage filtration at the back [2].

This study was conducted to provide additional information, with the main objective to investigate the relationship between cations and external carbon sources such as  $CH_3COOH$ , and the removal efficiency of TP on  $A_2/O$  and pre anoxic- $A_2/O$ . In this context, the following major issues were (i) the amount of injected external carbon source needed to obtain TP high removal efficiency, and (ii) the amount of injected external carbon source needed to discern the behavior of cations.

#### 2. Materials and methods

#### 2.1. Pilot-scale plant experiment

The pilot plant is located at the A-wastewater treatment plants in a city, Republic of Korea. This study was conducted over two operational periods and focused on (i) the relation between external carbon sources and TP removal efficiency from June 2010 to January 2011, and (ii) the relation between external carbon sources and cation behavior from February to May 2011.

Our experimental investigation used a pilot plant operated with  $A_2/O$  and pre anoxic- $A_2/O$  with  $CH_3COOH$ as the organic carbon source, and the pre anoxic phase was set up in front of the  $A_2/O$  process to improve nitrogen removal efficiency.

As mentioned previously, the external carbon source included  $CH_3COOH$ ,  $CH_3OH$ ,  $C_2H_5OH$ ,  $C_6H_{12}O_{6'}$  and so forth. Although methanol is commonly used currently, acetic acid was chosen as the external carbon source in this experiment. While methanol causes biological toxicity, there is no such risk with the use of acetic acid. In addition, as the ocean dumping of sludge was prohibited by the London Dumping Convention, anaerobic digestion of sludge in an effort to reduce the sludge volume may produce acetic acid in the process [7]. Despite its expenses, an acetic acid was chosen as the external carbon source.

The wastewater used was actual domestic wastewater taken from the overflow of primary settlement, and its flow rate was 10m<sup>3</sup>/day and was pumped into the anaerobic phase.

The process was operated under a solid retention time (SRT) of 28 d, and the average hydraulic retention time (HRT) was 2.0 h (Anaerobic and Pre anoxic), 3.5 h (Anoxic), 6.5 h (Aerobic), and 4.5 h (Second Settlement). SRT was controlled using sludge waste from the aerobic phase. The return ratio and internal return ratio were 50–100% (Qr/Q) and 100–300% (Qr/Q) respectfully. Table 1 lists the operating mode in this study.

Before beginning the study, a pilot plant operation was initiated with the  $A_2/O$  process to check the condition of the pilot plant. It turned out, however, that the concentration of total nitrogen (TN) was higher than expected, and the possibilities of studying TP properly were very low in consideration of the competition between PAOs and TN microbes. Thus, a pre anoxic phase was put before  $A_2/O$  to minimize the influence of

Table 1 Operating mode with and without injecting an external carbon source from the pilot plant

Mode	Process	Description
Mode 1	A <sub>2</sub> /O	A <sub>2</sub> /O
Mode 2	Pre anoxic - $A_2/O$	Pre anoxic - $A_2/O$
Mode 3	Pre anoxic - $A_2/O$	adding CH <sub>3</sub> COOH 0.7 mg/l to anaerobic phase
Mode 4	Pre anoxic - $A_2/O$	adding CH <sub>3</sub> COOH 2 mg/l to anaerobic phase
Mode 5	Pre anoxic - $A_2/O$	adding CH <sub>3</sub> COOH 4 mg/l to anaerobic phase

TN. From Mode 3 to 5, a study was conducted to check the efficiency of removing TP by injecting the external carbon source and, thus, to estimate the amount of the carbon source suitable for the targeted TP concentration. Although the documentation states that 2 mg Acetate/ l is necessary for 1 mg P release/l, there could be a difference between the theoretical amount and actual injection amount on site. Thus, a smaller amount of external carbon source than 4 ppm concentration was injected based on the theoretical function to find the most economical amount of external carbon source.

#### 2.2. Sampling procedure and analytical methods

The pilot plant was monitored through an analysis of pH, conductivity, temperature, Total Biological Oxygen Demand (TBOD), Soluble Biological Oxygen Demand (SBOD), Total Chemical Oxygen Demand (TCOD), Soluble Chemical Oxygen Demand (SCOD), Nitrate (NO<sub>2</sub><sup>-</sup>-N), Ammonia Nitrogen (NH<sub>2</sub>-N), Total Kjeldahl Nitrogen (TKN), Total Phosphate (TP), Soluble Phosphate (SP), Ortho-Phosphate (PO<sub>4</sub>), Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS), Total Solids (TS), Volatile Solids (VS), Sludge VolumeIndex (SVI), K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, and a particle size analysis. K<sup>+</sup>, Ca<sup>2+</sup> were measured with a Thermo scientific combination potassium electrode 9719BNWP and a combination calcium electrode 9720BNWP. Particle size analysis was measured with a LS particle size analyzer (Beckman Coulter). The other samples from each phase were analyzed according to the APHA Standard Methods (1998) 20th Edition [8], and all samples were determined by sampling between 10 to 11 A.M., two to three times every week.

# 3. Results and discussions

# 3.1. Behavior of phosphorus and Org-P in each mode

The results about external carbon source injection in each mode are as follows.

TP concentrations from influent were 4.0 mg/l, 3.71 mg/l, 3.72 mg/l, 3.62 mg/l, and 3.9 mg/l with an average of 3.79 mg/l. TP concentrations from effluent were 0.91 mg/l, 0.55 mg/l, 0.28 mg/l, 0.25 mg/l, and 0.13 mg/l. The efficiency of each mode was 76.8%, 85.3%, 92.2%, 93.1%, and 96.7%

The reason that the TP efficiency was highly variable in Mode 1 was that the pilot plant conditions did not remain steady.

In addition, we knew that although more of the external carbon source was injected in Mode 5 as compared with Mode 4, Mode 4 was more efficient than Mode 5. This may be because PAOs such as psychrophilic microbes have important advantages at low temperatures (below 20°C) [8,9]. Therefore, our results were possible since Mode 5 was conducted in the winter (2010.12 to 2011.01) (Fig. 1).

According to papers and documents, poly phosphate and organic phosphorus are more difficult to remove than orthophosphates in the chemical treatment [10].

Fig. 2 shows that the Org-P concentration in influent had an average of 0.117 mg/l, and the removal efficiencies of Org-P in each of the five modes by Biological Nutrients Removal (BNR) only were 74.57%, 88.89%, 90.24%, 92.02%, and 95.79%, respectfully.

It seems that the injection of an external carbon source was efficient for the removal of the Org-P. Thus, if a biological treatment is operated before a chemical treatment, the TP removal efficiency in the chemical treatment process that was operated after BNR will be able to be further increased.

# 3.2. Results of TP effluent on the C/P ratio in each mode

As described in the previous section, an external carbon source was injected sequentially in the pilot plant with concentrations of 0.7 ppm, 2 ppm, and 4 ppm from Mode 3, Mode 4, and Mode 5, respectfully. The amount



Fig. 1. Concentration of both influent and effluent and the removal efficiency of TP in each mode injected with an external carbon source.



Fig. 2. Concentration of Org-P of influent and the removal efficiency of Org-P in each mode injected with an external carbon source.

of carbon injected was determined by considering that 1 mg P release/l need 2 mg Acetate/l [11].

Because organic matter's concentration of domestic wastewater especially depends on an inflow time of wastewater, precipitation and rainfall-frequency, it was extremely variable in every mode, but the influent organic matter's concentration (especially SCOD) had an average of 153.03 mg/l. The C/P ratios under an external carbon source injection were 35.56 mg/l, 40.0 mg/l, 40.6 mg/l, 43.33 mg/l, and 42.57 mg/l from Mode 1 to 5, respectfully.

Because the external carbon source injected was a very little amount, the C/P ratio did not change dramatically. However, because the concentration of external carbon source injected was sufficient to increase the amount of P concentration released during the anaerobic phase, the P concentration absorbed in the aerobic phase increased (Fig. 3).

P concentration released by PAOs under the anaerobic phase increased. Due to this result, P concentration absorbed in aerobic phase increased more.



Fig. 3. Relation between the C/P ratio and TP of the effluent in each mode injected with an external carbon source.

In our pilot plant experiment, when we checked the released the P concentration in the anaerobic phase after injecting the carbon source, the high P-release was achieved 2.84 mg/l, 3.11 mg/l, 5.67 mg/l, 6.03 mg/l, and 6.66 mg/l, respectively, as SP concentrations.

# 3.3. Behavior of TN in each mode

Mode 1 and Mode 2 showed distinctive reductions of nitrogen whereas Mode 3, 4, and 5 did not. The reason is that the low temperatures degraded the activity of the denitrification bacteria.

It has been proposed by several investigators that because denitrification is affected by temperature, the lower the temperature is, the more efficiency of denitrification decreases.

Moreover, nitrate is a well-known inhibiting factor to the phosphorus release process in the anaerobic phase where COD is available [11] (Fig. 4).

In other words, denitrifying bacteria were considered to be able to respire rapidly and deplete the supply of organic substrates, such as short chain volatile acids (VFA), formed by the action of fermentative bacteria, in the anaerobic phase making the VFA no longer available for the PAOs. The amount of organic substrate that has to be used by PAOs for TP was reduced. More precisely, TN removal efficiency needed to be increased to increase the P-release in the anaerobic phase [12].

In spite of that, the TP concentration of effluent in Modes 3, 4, and 5 increased. The reason is that the PAOs was lower-range mesophiles or psychrophiles and predominated only at 20°C or possibly lower.

## 3.4. Behavior of cations in each mode

The result of the behaviors of  $K^+$  and  $Ca^{2+}$  were that when more of the external carbon source was injected, the more cations were released in the anaerobic phase,



Fig. 4. TN removal efficiency with an injection of external carbon source and the influent concentration of TN in each mode.

and the absorption of cations in the aerobic phase increased significantly by 16.35%, 25.72%, 31.2%, and 63.69%. This means that the external carbon source injection increased P- uptake concentration under the aerobic phase, and we can expect to increase the TP removal efficiency in effluent.

This principle could be utilized in adjusting the amount of external carbon source injection. Injection of an external carbon source into the influent may increase the concentration of PO<sub>4</sub> during the anaerobic phase, which will result in the increase of K<sup>+</sup> concentration in that phase. In reference to the data on the increase of K<sup>+</sup> concentration, the PO<sub>4</sub> concentration within the anaerobic phase can be estimated, and theoretically the PO<sub>4</sub> absorbed in the aerobic phase would be more than the release of PO<sub>4</sub> within the anaerobic phase. Thus, the approximate amount of PO<sub>4</sub> absorbed in the aerobic phase could be predicted, which would be the concentration of  $TP_{eff}$ . If the release of  $PO_4$  in the anaerobic phase is so insufficient that TP<sub>eff</sub> does not meet the wastewater standard, it will be necessary to increase the injection of the external carbon source into the anaerobic phase [13,14]. However, an attempt to accumulate specific data on this principle is in progress currently (Fig. 5).



Fig. 5. Behavior of cations in each mode injected with an external carbon source: (a) the behavior of  $K^{2+}$  and (b) the behavior of  $Ca^{2+}$  (An: anaerobic, Ax: anoxic, Ox: oxic, RAS: return activated sludge).

# 4. Conclusions

When the BNR process with an external carbon source was operated, the removal efficiency of the TP in the effluent was a maximum of 94.48%. Moreover, a large quantity of Org-P, which is difficult to be removed by chemical treatment, was removed considerably. Therefore, if a biological treatment is operated before a chemical treatment, it is possible to further increase the TP removal efficiency in the chemical treatment process.

Our study also found that, some of the external carbon source affected nitrogen removal. Metal cations can be great parameters which predict the exact amount of the external carbon source that needs to be injected. We also found that injecting an external carbon source directly during the anaerobic phase increased the concentration proportionally, which meant that  $K^+$ , and  $Mg^{2+}$  can be considered parameters to control the amount of external carbon which has to be injected. Therefore, the TP treatment process with BNR meets the criteria of effluent quality and is a cost-effective and environmentally sound alternative compared to a chemical treatment.

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