

Application of Iron Electrolysis to Full-Scale Activated Sludge Process for Phosphorus Removal

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ABSTRACT

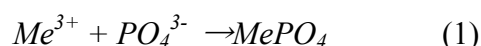
Addition of coagulant to the activated sludge process is an effective method to remove phosphorus from wastewater. Recently, iron electrolysis method has been developed as a new methodology of addition of coagulant into the activated sludge process. Although this process has been applied to industrial wastewater treatment plants or small-scale domestic wastewater treatment plants, the phosphorus removal performance by iron electrolysis combined with full-scale activated sludge process has not been clear yet. The objective of this study is to investigate the phosphorus removal efficiency by iron electrolysis combined with the activated sludge process. The enhanced biological phosphorus removal took place and phosphorus removal efficiency was increased without iron addition because of the occurrence of anaerobic condition in the surveyed wastewater treatment plant. Phosphorus removal performance in the investigated wastewater treatment plant was improved by the iron electrolysis. Effluent phosphorus concentration was decreased below 1.0 mg/L with additional iron of Fe/P molar ratio 0.4. The theoretical weight of iron release agreed with the actual weight decrease of iron electrodes. The introduction of iron electrolysis to the activated sludge process could enhance the phosphorus removal efficiency without any effects on substrate removal performance and make the phosphorus removal to be stable and sustainable.

Keywords: activated sludge process, iron electrolysis, phosphorus removal

INTRODUCTION

In order to control the eutrophication in lakes and estuaries, phosphorus removal processes have been introduced in wastewater treatment plants. The activated sludge process with coagulant addition and the enhanced biological phosphorus removal (EBPR) process have been widely used in sewage treatments (Janssen *et al.*, 2002). Although the EBPR process can remove phosphorus with low cost, phosphorus removal performance is sometimes decreased by the disappearance of anaerobic condition caused by the decrease of BOD load or inflow of nitrate (Choi *et al.*, 2001; Kazmi *et al.*, 2001; Merzouki *et al.*, 2001; You *et al.*, 2004). The activated sludge process with coagulant addition can remove phosphorus stably, but it has some problems such as the production of large amount of excess sludge as well as the high cost of coagulant addition. Therefore, the combination of these two processes seems to be practicable.

It is generally known that phosphorus removal with coagulant results from the formation of metal phosphate salts as follows (Metcalf and Eddy Inc., 1991),



However, a coagulant addition of more than 1 molar ratio to influent phosphorus load is required because a fraction of coagulant ion combines with hydroxide ion to form a

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hydroxide compound. In addition, Fe^{3+} , Al^{3+} and PO_4^{3-} are in small fractions at neutral pH (Rittmann and McCarty, 2001; Mishima and Nakajima, 2003a). The precise mechanism of phosphorus removal in the activated sludge process has not been cleared yet.

Recently, iron electrolysis method (shown in Fig. 1) has been developed as a new methodology for the addition of coagulant into the activated sludge process (Moriizumi *et al.*, 1999, 2000, 2001). Ferrous ions are supposed to be released from the anode of the iron electrodes and then oxidized by dissolved oxygen to become ferric ions. These ferric ions combine with phosphate ions to remove phosphate from wastewater. It is known that iron oxides formed in the anode sometimes prevent the iron electrode from dissolving. This problem was clarified by interchanging the anode and the cathode in several periods (Moriizumi *et al.*, 1999). The process was applied to the industrial wastewater treatment plants or small-scale domestic wastewater treatment plants. However, it is not clear that the iron electrolysis combined with the activated sludge process can efficiently remove phosphorus in full-scale wastewater treatment process, especially sequencing batch reactor process. Moreover, the determination of the optimum amount of iron addition to the activated sludge process has not been understood well. In this study, the availability of the iron electrolysis method to the activated sludge process is discussed by employing this method in an actual wastewater treatment plant.

MATERIALS AND METHODS

Operational conditions of the investigated plant

The domestic wastewater treatment plant for 1,100 p.e. was investigated. The plant consisted of two SBR (sequencing batch reactor) tanks (SBR1 and SBR2). The volume of each tank was 173 m^3 . They were operated with 6 h cycle of 1 h reaction (mixing followed by aeration) $\times$ 3 times, 1 h settling and 2 h discharge. The influent of 32 m^3 was allowed to flow from the beginning of the mixing phase for about 80 min. The flow of the treatment process is shown in Fig. 2.

Iron electrolysis equipment with a volume of 130 L was installed only on SBR1 tank. It had 32 iron electrodes (16 units) as shown in Fig. 3. The mixed liquor in SBR1 was pumped into the iron electrolysis equipment using the submerged pump (100 L/min) then returned back into SBR1 from the beginning of mixing phase of the SBR during the electrolysis time as shown in Table 1. The submerged pump was completely stopped during the settling and the discharge phases. Iron was added as coagulant to the mixed

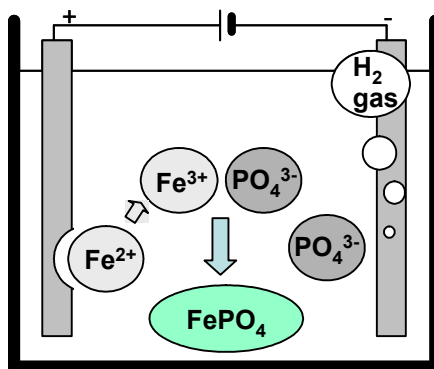


Fig. 1 - Iron electrolysis method.

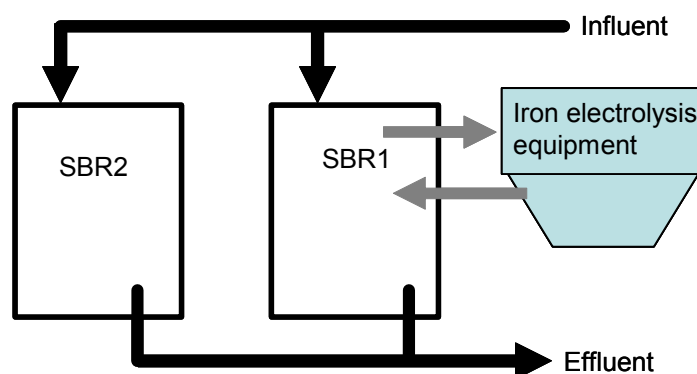


Fig. 2 - Flow of the treatment process.

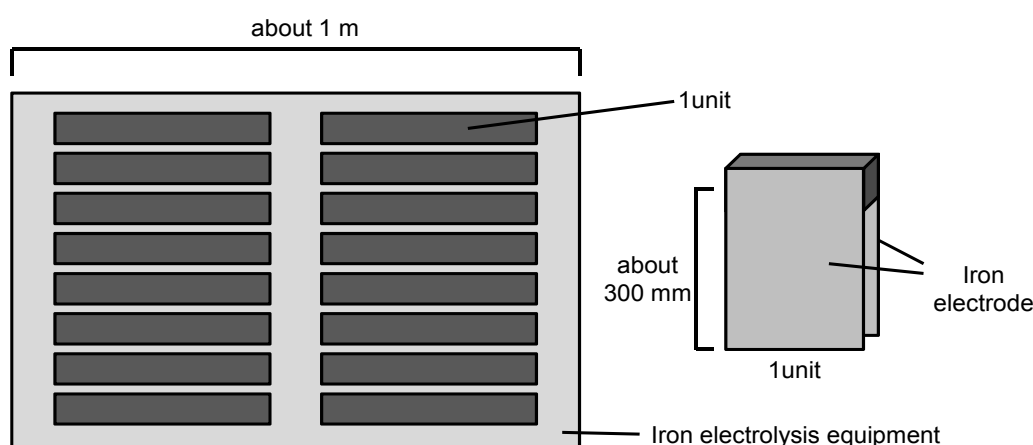


Fig. 3 - Schematic representation of iron electrolysis equipment.

Table 1 - Conditions of electrolysis.

	Run1	Run2	Run3	Run4
Fe/P molar ratio	0	0.1	0.2	0.4
Current (A)	-	0.86	0.86	2.1
Electrolysis time in one SBR cycle (h)	-	1.5	3.0	3.0

liquor in the iron electrolysis equipment by controlling the amount of the electric current. The molar ratios of the added Fe to influent phosphorus were set at 0, 0.1, 0.2 and 0.4 in SBR1 (Run1, Run2, Run3 and Run4, respectively) as shown in Table 1. In the iron electrolysis equipment, the mixed liquor was continuously aerated in order to prevent anaerobic condition. The SBR2 was operated without iron electrolysis as a control experiment.

Analytical methods

Influent, effluent, activated sludge in SBR1 and SBR2, and supernatant liquor of the thickener were sampled in about every 10 days interval. Concentrations of MLSS, MLVSS, T-P, PO₄-P, T-N, NO₃-N, T-Fe and D-Fe in the activated sludge were measured.

Dehydrogenase activity and oxygen uptake rate of the activated sludge were also observed. As for the influent and the effluent, SS, BOD, T-P, PO₄-P, T-N, NO₃-N and T-Fe were measured. Concentrations of SS and T-Fe in the supernatant liquor of the thickener were also measured. Iron was determined by an inductively coupled plasma emission spectrometry (Seiko SPS4000) after the digestion of organics using nitric acid and hydrogen peroxide. Nitrate-nitrogen was determined by high performance liquid chromatography method. The other water quality parameters were determined according to JIS K0102.

RESULTS AND DISCUSSION

Characteristics of the influent

The actual influent flow was 210 ± 21 m³/d. The mean value and the standard deviations of SS, BOD, T-N and T-P concentrations of the influent (in the stabilization tank) during Run1 to Run4 are shown in Table 2. The mean values of SS, BOD, T-N and T-P concentrations were 120 mg/L, 210 mg/L, 43 mg/L and 4.5 mg/L, respectively. These were approximately the same concentrations as those of the conventional Japanese wastewater. The standard deviations of SS and BOD concentrations were large but those of T-N and T-P concentrations were small. The average alkalinity of the influent was 160 mg/L.

Although the supernatant liquor of the thickener was turned back to the stabilization tank, T-Fe concentration in it was usually less than 1.0 mg/L and it did not affect the T-Fe concentration in the influent.

Outline of the treatment performance

The SS, BOD and T-N concentrations (average $\pm$ SD) in the effluent of SBR1 and SBR2 are shown in Table 3. There was no difference in the removal performance of SS, BOD, and T-N between SBR1 and SBR2. The average removal efficiencies for SS, BOD, and T-N in both SBRs were 97%, 98% and 91%, respectively. The SS, BOD and T-N were effectively removed from the wastewater. The average concentrations of MLSS in SBR1 and SBR2 were 3,300 mg/L and 3,700 mg/L, respectively. The ratio of MLVSS to MLSS was 80% and was stable in both SBRs.

Table 2 - Characteristics of the influent (mg/L).

SS	BOD	T-N	T-P
120 $\pm$ 45	210 $\pm$ 62	43 $\pm$ 8.4	4.5 $\pm$ 0.35

Table 3- SS, BOD and T-N concentrations in the effluent.

	SS (mg/L)	BOD (mg/L)	T-N (mg/L)
SBR1	3.8 $\pm$ 6.4	4.0 $\pm$ 5.4	3.9 $\pm$ 1.9
SBR2	3.8 $\pm$ 2.5	3.0 $\pm$ 4.7	3.5 $\pm$ 2.8

Fe release by iron electrolysis

All iron electrodes were replaced by new ones after the end of Run3. The weight of theoretical iron release from the electrodes was calculated by Faraday's Law (Equation 2), where I was the electric current (A), T was the electrolysis time (s), F was the Faraday constant and 55.85 was the atomic weight of iron.

$$Fe \text{ weight (kg)} = I \cdot T \cdot 16 \cdot 55.85 / (2 \cdot F \cdot 1000) \quad (2)$$

The actual weight decrease of iron electrodes was estimated by the difference of the weight between the new and the used iron electrodes. The theoretical release and actual weight decrease were 30 kg and 34 kg, respectively. The actual weight decrease of iron was close to the theoretical weight release. The results indicated that Fe was effectively added to the activated sludge process by iron electrolysis.

On the other hand, the cost is estimated by the electric power consumption calculated from the current and the voltage. The electric power consumption for the electrolysis at Run4 was estimated to be less than 800 W.

Phosphorus removal

The change of effluent T-P concentration in each SBR is shown in Fig. 4. Effluent T-P concentration in SBR2 was 1.5 - 2.0 mg/L and phosphorus was comparatively removed well without Fe addition. In Run2, influent BOD concentration was high and effluent $\text{NO}_3\text{-N}$ concentration was low compared with the other runs. Therefore, it was suggested that anaerobic condition was kept and phosphorus was released from activated sludge bacteria in the anaerobic phase. From these, it was thought that the EBPR took place and effluent phosphorus was decreased.

The average concentrations of effluent T-P in SBR1 and SBR2 for Run1 to Run4 are shown in Table 4. Effluent T-P concentration in SBR1 was in the same range as that in SBR2 during Run1, however, the concentration decreased to less than 1.0 mg/L during Run2 ($\text{Fe/P} = 0.1$). Effluent T-P concentration in SBR1 during Run2 was also less than that of Run3 ($\text{Fe/P} = 0.2$) and Run4 ($\text{Fe/P} = 0.4$). In Run2, it was thought that EBPR took place as in SBR2. Therefore, phosphorus was well removed by the combination of

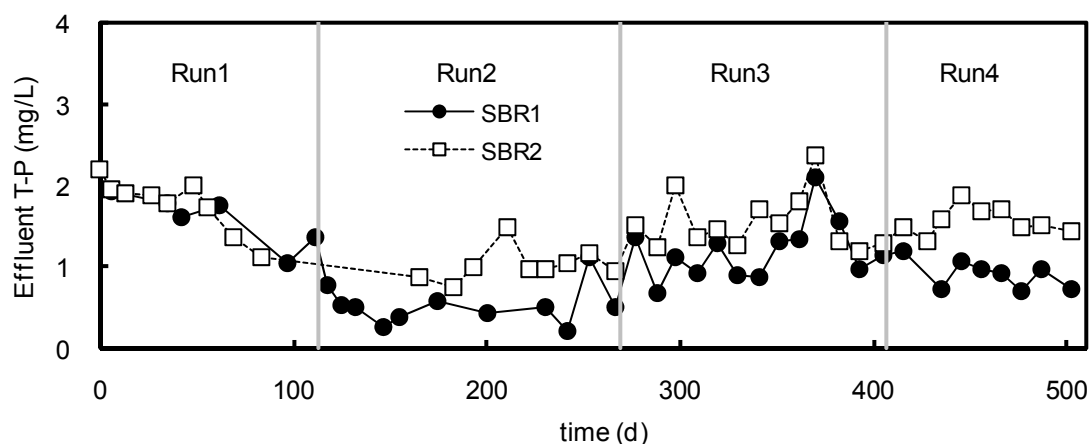


Fig. 4 - Change of effluent T-P.

Table 4 - Average effluent T-P concentrations in SBR1 and SBR2 (mg/L).

	Run1	Run2	Run3	Run4
SBR1	1.6 ± 0.32	0.50 ± 0.28	1.2 ± 0.38	0.89 ± 0.15
SBR2	1.8 ± 0.34	1.0 ± 0.21	1.5 ± 0.35	1.6 ± 0.17

EBPR and coagulation processes. There was a difference between the effluent T-P concentrations in SBR1 and SBR2 during Run3. In Run4, the difference was larger. Moreover, average effluent $\text{PO}_4\text{-P}$ concentration in SBR1 was 0.76 mg/L and always less than 1.0 mg/L in Run4. This indicated that the phosphorus removal performance was enhanced by iron electrolysis.

Nakajima and Mishima (2004) reported that about 1.5 molar ratio of Fe to influent phosphorus was needed to get the phosphorus concentration in the effluent below 1.0 mg/L by the iron electrolysis method without EBPR in the laboratory-scale experiment. Mishima and Nakajima (2010) reported that the Fe/P molar ratio for phosphorus removal could be reduced to 0.2 - 0.5 with EBPR in the laboratory-scale SBR experiment. In this study, it was found that the phosphorus removal could be done with a small Fe/P molar ratio even in the full-scale wastewater treatment process when EBPR took place.

On the other hand, Mishima and Nakajima (2003b) pointed that a large amount of phosphorus to Fe could be removed in the case that the Fe/P molar ratio was small, like 0.05 - 0.1. In Run2, the Fe/P molar ratio was 0.1, therefore, it seemed likely that a large amount of phosphorus to added Fe was effectively removed.

The molar ratio of added Fe to effluent T-P in SBR2 was calculated as the molar ratio of Fe to phosphorus for the removal by iron electrolysis except for biological phosphorus removal. The relationship between this molar ratio and the difference of effluent T-P concentrations in SBR1 and SBR2 is shown in Fig. 5. The approximation line except Run2 is also shown in Fig. 5 and the difference of effluent T-P concentrations increased in a straight line as the molar ratio increased. This result indicated that phosphorus removal had been accomplished biologically and chemically, and the amount of chemical phosphorus removal was decided in proportion to the amount of added Fe by iron electrolysis.

Phosphorus release and uptake

Changes of $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ concentrations during mixing and aerobic phases of Run3 in SBR1 on 362nd day and 382nd day are shown in Fig. 6. Mixing and aerobic conditions were repeated three times in one SBR cycle. Influent was allowed to flow for about 80 min from the beginning and lasted within the second mixing condition of that cycle. On the beginning of the first mixing phase, $\text{NO}_3\text{-N}$ remained on 362nd day. At the latter half of the first mixing phase, $\text{NO}_3\text{-N}$ was removed by denitrification and the anaerobic condition took place. However, $\text{NO}_3\text{-N}$ always existed after the first aerobic phase on 362nd day. Phosphorus increased during the first mixing phase and decreased during the first aerobic phase. After the second mixing phase, $\text{PO}_4\text{-P}$ did not increase by the release from activated sludge bacteria and was constant because of these aerobic and

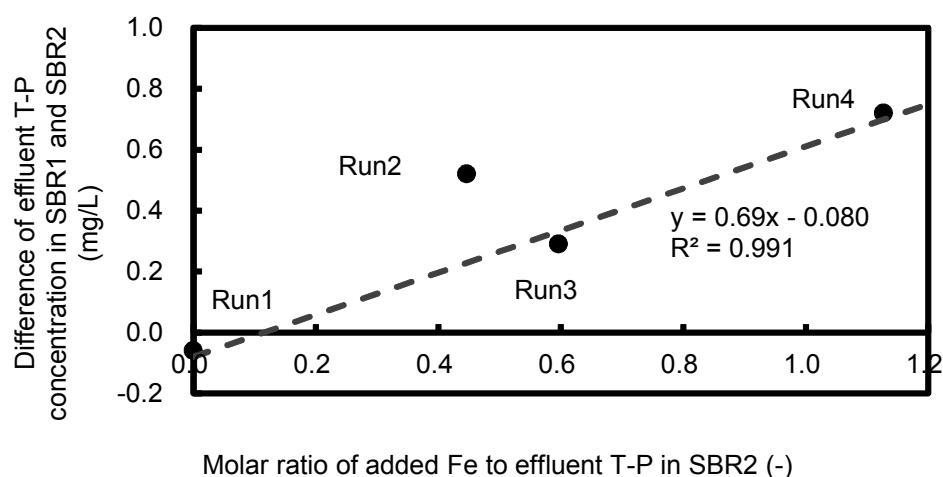


Fig. 5 - Relationship between molar ratios of added Fe to effluent T-P in SBR2 and difference of effluent T-P concentrations in SBR1 and SBR2.

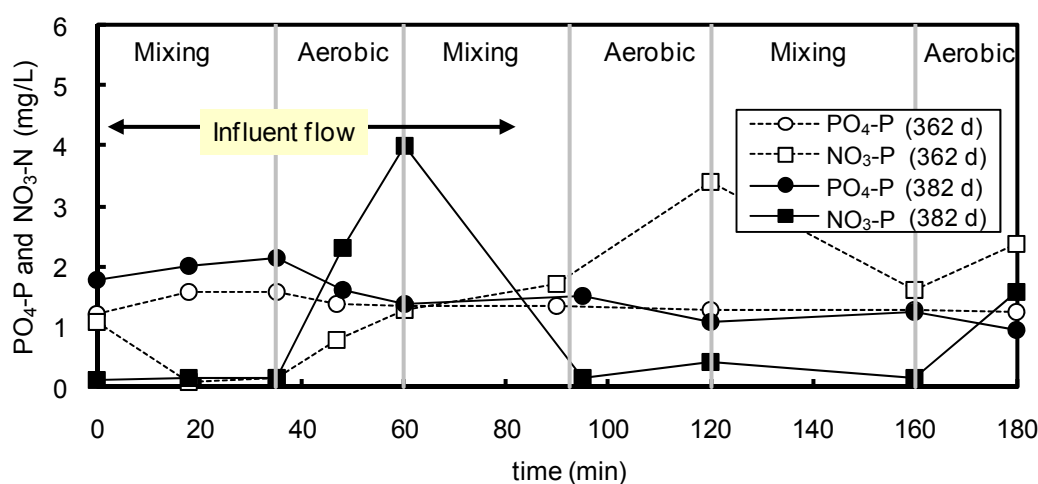


Fig. 6 - Change of $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ during mixing and aerobic phases in SBR1.

anoxic conditions. These results agreed with Kuba *et al.* (1993, 1994), Arnz *et al.* (2001) and Rieger *et al.* (2001) reporting that the phosphorus release did not occur if $\text{NO}_3\text{-N}$ was present.

On the other hand, at the beginning of the first mixing phase, $\text{NO}_3\text{-N}$ did not remain on 382nd day. At the first aerobic phase, $\text{NO}_3\text{-N}$ increased by nitrification on 382nd day. However $\text{NO}_3\text{-N}$ was then maintained low by denitrification and anaerobic condition took place in the mixing phase. Phosphorus increased during the first mixing phase and decreased during the first aerobic phase. Phosphorus at the end of the third aerobic condition of 382nd day was lower than that of 362nd day, while $\text{PO}_4\text{-P}$ at the end of the first mixing condition of 382nd day was higher than that of 362nd day. These results indicate that the occurrence of the anaerobic condition without $\text{NO}_3\text{-N}$ enhanced the phosphorus removal efficiency.

The influent BOD concentrations on 362nd day and 382nd day were 200 mg/L and 260 mg/L respectively, showing that the latter was higher than the former. It was suggested that high carbon source induced denitrification in the mixing phase which caused the anaerobic conditions, resulting in high phosphorus removal.

Fe content in the activated sludge

The Fe content in the activated sludge (CFe; mg/g) was calculated by the equation.

$$CFe = (T-Fe - D-Fe) / MLSS \cdot 1000 \quad (3)$$

where, T-Fe and D-Fe are the total and dissolved Fe concentrations in the mixed liquor (mg/L). The change of CFe is shown in Fig. 7. The average CFe during Run1 in SBR1 and Run1 – Run4 in SBR2 was about 2 mg/g and almost constant. However, CFe during Run2 - Run4 in SBR1 increased since the beginning of each run and became constant later. The average CFe during Run2, Run3 and Run4 in SBR1 were 4.5 mg/g, 8.9 mg/g and 16 mg/g, respectively. The CFe was increased by the iron electrolysis in proportion to the molar ratio of added Fe to the influent phosphorus load.

Mishima and Nakajima (2003b) reported that CFe can be calculated by equation (4), where u is the amount of Fe to be added into the activated sludge (mg/d), S is the total SS amount in the aeration tank (g) and CFe_0 is the CFe at the beginning of the operation (mg/g).

$$CFe = u \cdot SRT / S + (CFe_0 - u \cdot SRT / S) \cdot \exp(-t / SRT) \quad (4)$$

The change of CFe during Run2 - Run3 calculated by equation (4) is shown in Fig. 7, where SRT was estimated by the calculation of the balance of phosphorus. In general, the calculated CFe agreed with the measured one. This indicated that CFe can be estimated by equation (4). Mishima and Nakajima (2003a, 2003b) and Nakajima and Mishima (2004) pointed that the added coagulant into the activated sludge became insoluble in the form of iron hydroxide or iron oxide and accumulated in the aeration tank without being discharged in the effluent. They also mentioned that phosphorus from wastewater was removed by insoluble coagulant as a part of activated sludge. Therefore, it will be useful

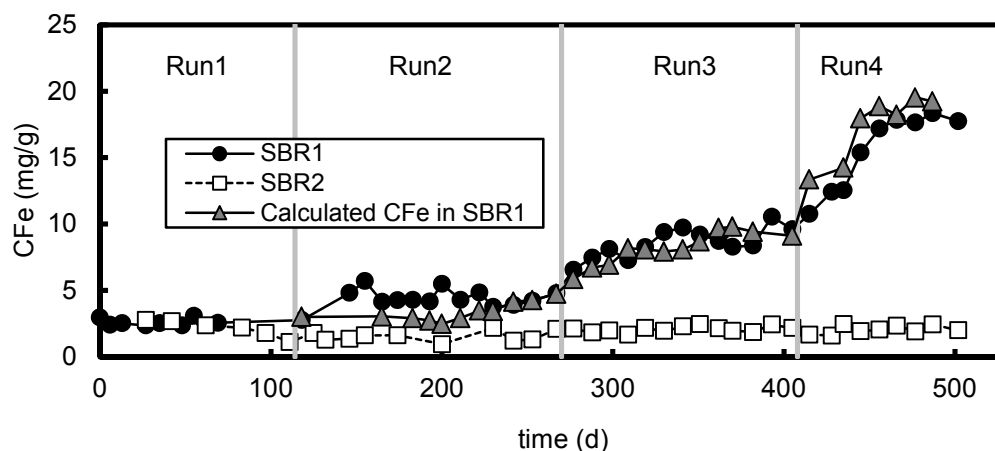


Fig. 7 - Change of CFe in SBR1 and SBR2.

for the operation of activated sludge process for phosphorus removal to predict the change of CFe.

Respiratory activity of activated sludge

Dehydrogenase activity and oxygen uptake rate (OUR) of the activated sludge in SBR1 and SBR2 were measured to observe the effect of the iron electrolysis method on the substrate removal performance. Before the measurement of both respiratory activities, the supernatant of activated sludge was replaced by glucose solution of BOD 200 mg/L. The respiratory activities in SBR1 and SBR2 are shown in Fig. 8. Although some differences were found among the four runs, there was no fundamental difference between SBR1 and SBR2 in each run.

The dominant protozoa and metazoa in the activated sludge were *Aspidisca* sp., *Vorticella* sp., *Philodina* sp. and others, indicating a good performance of sedimentation of activated sludge. These indicated that the iron electrolysis method had no negative effect on the substrate removal performance of the activated sludge process.

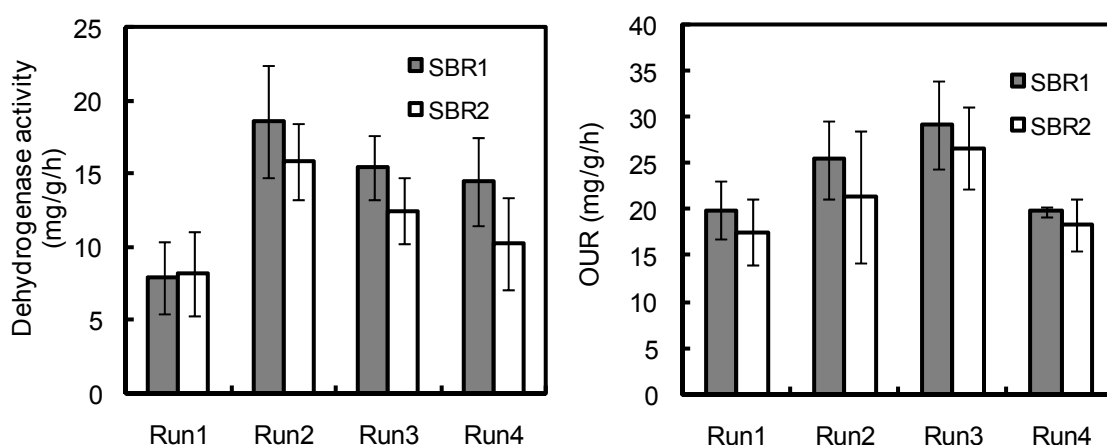


Fig. 8 - Dehydrogenase activity (left) and OUR (right) in SBR1 and SBR2.

CONCLUSIONS

In this study, phosphorus removal performance with iron electrolysis method was evaluated from the investigation of full-scale wastewater treatment plant. The EBPR process took place and the phosphorus removal efficiency was increased without Fe addition because of the disappearance of $\text{NO}_3\text{-N}$ in anaerobic condition. Phosphorus removal performance was improved by the introduction of iron electrolysis in the activated sludge process. The fact that the actual weight of iron decrease by electrolysis agreed to the theoretical value, it indicated effective Fe addition to the activated sludge. Effluent phosphorus concentration was decreased below 1.0 mg/L by the Fe addition with Fe/P molar ratio of 0.4. The introduction of iron electrolysis to the activated sludge process has no negative effect to its substrate removal performance.

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