

Improvement of Phosphorus Removal by Calcium Addition in the Iron Electrocoagulation Process

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Abstract

Small-scale wastewater treatment plants (SWTPs) are widely used as decentralized wastewater treatment systems in sparsely populated areas of Japan. Iron electrolysis, an electrocoagulation technology, is installed in these SWTPs for phosphorus removal. Phosphorus can be removed via the formation of an insoluble compound containing phosphate and iron like FePO_4 ; however, it was necessary to determine the conditions under which phosphorus can be effectively and stably removed in actual SWTPs. According to previous studies using iron compounds, improved phosphorus removal was obtained by Ca addition. It is therefore thought that calcium addition may also be effective in improving the phosphorus removal during iron electrolysis in SWTPs. It is also important to determine the chemical state of iron to understand the phosphorus removal mechanism during iron electrolysis. In this study, laboratory-scale batch experiments with the iron electrolysis method were conducted to investigate the effect of phosphorus removal using treated wastewater from actual SWTPs without or with Ca addition. The results indicated that the addition of Ca improved the phosphorus removal performance. Furthermore, phosphorus removal was inhibited in the presence of high DOC. The X-ray absorption fine structure measurements of the produced particulates in the experiments showed no substantial change in the chemical state of iron without or with Ca addition. The statistical analyses revealed the range of improving or inhibiting effects on phosphorus removal owing to the Ca and DOC. Thus, the results of this study provided useful information pertaining to the influence of coexisting substances on phosphorus removal and the chemical state of iron in the produced particulates.

Keywords

Calcium addition; iron electrolysis; phosphorus removal; X-ray absorption fine structure

INTRODUCTION

Small-scale wastewater treatment plants (SWTPs) are referred to as Johkasou systems in Japan. They treat domestic wastewater from fewer than 10 household directly. Hence, they are widely used as decentralized wastewater treatment systems in sparsely populated areas of Japan. Iron electrolysis was developed and used as a method for advanced SWTPs to remove phosphorus. Iron electrolysis is a type of chemical coagulation method (Mollah et al., 2001; Pulkka et al., 2014) that uses electrochemical technology (Cong et al., 2016) installed in the SWTPs. The iron electrolysis method was applied to various wastewater treatment processes for phosphorus removal (İrdemez et al., 2006; Mishima et al., 2011; Tran et al., 2012). It is possible to elute iron from the anode by energizing an iron electrode, which is inserted into an aerobic tank in the SWTPs for phosphorus removal. This enhances the combination of iron and phosphorus, thereby forming FePO_4 , which performs the removal of phosphorus from wastewater. The low-cost iron plate can be held in the aerobic tank in this plants, and therefore it is not necessary to mount a flocculants tank separately as in the case of a large-scale treatment plant. In addition, this technique is useful for small-scale wastewater treatment since there is no decrease in the pH due to the production of H_2 gas in the cathode.

It is known that the metal-salts addition into wastewater treatment process is 1.5-2.5 times the stoichiometric amount and Fe/P of 2 is required to provide an effluent with 1 mgP/L (Rittmann and McCarty, 2001). However, the precise mechanism of phosphorus removal by the iron electrolysis method has not been clarified, yet. Furthermore, instances of unsatisfactory performance with respect to the phosphorus removal based on wastewater plants have been reported. Nevertheless, the effect of phosphorus removal was improved by adjusting the operating conditions such as increasing the amount of iron electrolysis. However, increasing the amount of electrolyzed iron leads to an acceleration of iron electrode depletion. Therefore, it is necessary to develop the better operational method to stabilize phosphorus removal in SWTPs with iron electrolysis.

Conversely, the chemical states of elements in materials can be estimated by using an x-ray absorption fine structure (XAFS) technique. The XAFS spectrum can be divided into two regions, namely the x-ray absorption near-edge structure (XANES) and the extended x-ray absorption fine structure. The chemical states of the elements in the sample can be estimated by comparing the XANES of the sample with those of standard reference materials or other samples. Recently, XAFS measurement was applied to environmental samples (Takaoka et al., 2008; Hasan et al., 2012; Ishiwatari et al., 2013). The XAFS spectra of liquid samples can also be directly measured, and the measurement is possible even in amorphous materials. Therefore, XAFS measurements can obtain useful information for phosphorus removal on the state of iron in the sample from the iron electrolysis method.

It is also important to consider the impact of coexisting materials in the wastewater on the removal of phosphorus. For example, according to Li et al., (2013), improved phosphorus removal was achieved by the addition of calcium using iron compounds. An improvement in the phosphorus removal performance was also reported by using the iron electrolysis method in Ca-rich conditions (Moriizumi et al., 1999). Hence, it was assumed that calcium addition could also be effective in improving phosphorus removal during iron electrolysis in SWTPs. Thus, further improvement of phosphorus removal by the present method necessitates elucidating the impact of the present method on the phosphorus removal of coexisting materials such as Ca in the wastewater.

Based on the abovementioned points, this study aimed to improve the phosphorus removal performances by the addition of calcium in the iron electrolysis method in SWTPs. However, various factors such as the loading rate of phosphorus, the amount of wastewater, the amount of the iron supplied during the electrolysis, and the phosphorus release from the stored sludge influence phosphorus removal in actual SWTPs. Hence, in this study, the effluents from actual SWTPs were collected and filtered to conduct laboratory-scale batch experiments using the filtered effluent and the electrolysis equipment. It is possible to directly evaluate the effect of water quality on phosphorus removal using the iron electrolysis methods in these experiments. This study focused on the influence of Ca as an effective coexisting substance in phosphorus removal empirically. Improvements and deteriorations in phosphorus removal were investigated, and statistical analyses methods were employed to estimate the extent of the impact of these changes. Furthermore, the XAFS measurement of the produced particulates was performed to discuss the chemical state of iron with respect to these effects.

MATERIALS AND METHODS

Targeted actual SWTPs with iron electrolysis

This study targeted 18 actual SWTPs with the iron electrolysis method. The SWTPs consisted of 8 for 5 people equivalent (p.e.), 8 for 7 p.e., and 2 for 10 p.e. As shown in Figure 1, each plant had an aerobic tank and two anoxic tanks. For example, the volumes of the aerobic tank, anoxic tank 1, and

anoxic tank 2 were 0.73 m³, 0.93 m³, and 0.95 m³, respectively, at the plant for 5 p.e. Fluidized media were installed in the aerobic tank for biological treatment and biofilm filtration. The oxidation of organic matter and nitrogen occurred in the aerobic tank. The wastewater in the aerobic tank was returned to the first anoxic tank for denitrification. Four iron electrodes (two units) were installed in the aerobic tank with continuous aeration. The weight of each iron electrode was approximately 1.2 kg. Direct current was allowed to flow to supply the iron ions into the aerobic tank for phosphorus removal. Backwashing was performed by strong aeration twice daily to send the produced sludge from the aeration tank to anoxic tank 1. The biologically and chemically produced sludge was stored in the anoxic tank 1.

Conditions of laboratory scale experiments

A total of 55 effluent samples were collected. This was followed by measuring biological oxygen demand (BOD), suspended solids, pH, dissolved organic carbon (DOC), NH₄-N, NO₂-N, NO₃-N, PO₄-P, and alkalinity. A phosphate solution was added to each filtered sample and the phosphorus concentration was adjusted to 5 mg/L. A filter paper with a pore size of 1.0 µm was used for filtration. Then, the samples with a volume of 200 mL were placed in a tall beaker and two iron electrodes (120 mm × 20 mm × 2 mm) were installed above the beaker, as shown in Figure 2. Aeration and mixing were conducted at the bottom of the beaker. The iron electrodes were connected with a constant current power supply (PMC35-1A; Kikusui Electronics Corp.). A direct current of 0.014 A was allowed to flow for 15 min. The current was monitored using an ampere meter. Samples were taken from the beaker and were then filtered after 0 min, 3.8 min, 7.5 min, 11 min, and 15 min. The phosphorus concentrations in each filtrate were measured. After 15 min, Faraday's law was used to calculate the molar ratio of the iron supplied from the electrolysis to the phosphorus in the bulk solution, that is, Fe/P molar ratio = 2.0. Additionally, one mL of calcium solution (2000 mg/L) was added to the samples prior to the batch experiments to evaluate its effect on phosphorus removal in order to increase Ca concentration in the samples by 10 mg/L. The phosphorus concentration against Fe/P molar ratio or Ca concentration was compared from the experimental results. Pearson's correlation analysis and multiple regression analysis were performed for each of the water qualities with PO₄-P concentrations. SPSS 22.0 statistics software (SPSS Inc.) was used for the statistical analyses.

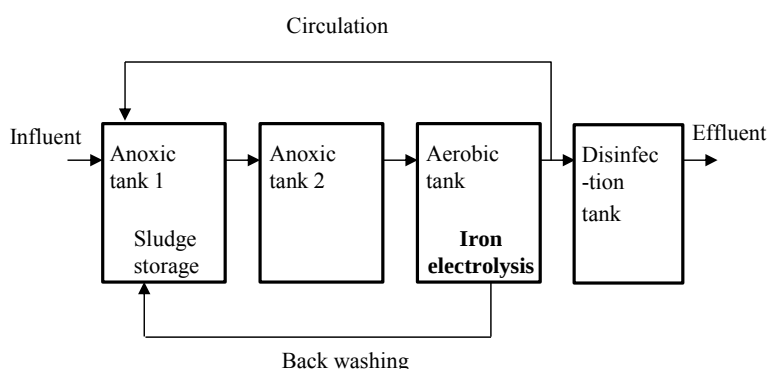


Figure 1. Treatment process of investigated SWTPs with iron electrolysis.

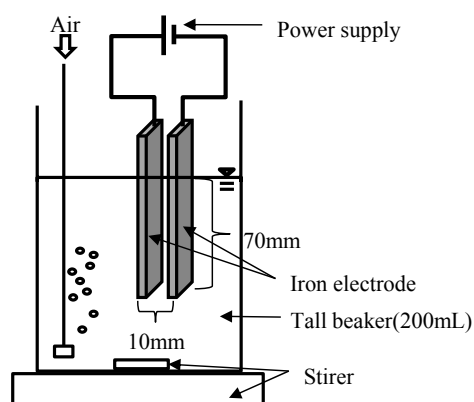


Figure 2. Schematic diagram of the laboratory scale experiment.

Conditions of XAFS measurements

A pore size of 1.0 µm was used to filter the solutions obtained after performing the above batch experiments with Fe/P molar ratio of 1.0, and the chemically produced particulates were collected on the filter. The samples were oven-dried and the XAFS spectra were measured. XAFS

measurements were performed at the Synchrotron Radiation Center of Ritsumeikan University, Japan, to characterize the chemical form of iron in the collected particulate samples. The Fe K-edge XAFS spectra were measured using BL-3 at the above mentioned facility, which was equipped with a Si (220) double-crystal monochromator (Ishiwatari et al., 2013). The samples were measured by fluorescence yield mode using an ionization chamber filled with mixed gases. These gases included 15% Ar and 85% N₂ in the incident chamber and 50% Ar and 50% N₂ in the transmission chamber (Takeuchi et al., 2011). A three-elements Ge solid-state detector (Canberra) was used as the fluorescence detector in accordance with experiments conducted in previous studies by Asaoka et al., (2012) and Mishima et al., (2016). For all the samples, the obtained spectra were normalized by the intensity obtained at 7300 eV. The pre-edge background contribution was subtracted from the raw XAFS spectra obtained in the fluorescence yield mode by removing a constant extrapolated from the pre-edge region. The commercially provided software (REX2000 ver. 2.5.93; Rigaku Co., Ltd.) which was often used for the analysis of the XAFS spectra (Kodama et al., 2006; Takahashi et al., 2013; Moroki et al., 2014) was also used in this study. The R factors (%) were calculated based on the least squares fitting method by using the following equation, where *I*_{without} and *I*_{with} denote the observed intensities in the XAFS spectra obtained from the batch experiment without and with Ca addition, respectively.

$$R = \frac{\sum (I_{\text{without}} - I_{\text{with}})^2}{\sum I_{\text{without}}^2} \times 100$$

RESULTS AND DISCUSSION

Outline of phosphorus removal in experiments

The experiments were conducted using 55 samples of treated water from actual SWTPs. Table 1 shows the average water quality levels, standard deviation, minimum values, and maximum values of the treated water after adjusting PO₄-P concentration. The organic substances were well removed in the SWTPs as the BOD and DOC averages were low. However, a maximum DOC of 20 mg/L was also observed. With respect to the nitrogen, NO₃-N was much higher than NH₄-N. This suggested that denitrification was the rate-limiting step in the whole nitrogen removal. The Ca concentration ranged from 11 mg/L to 45 mg/L, with an average Ca concentration of 21 mg/L. The average PO₄-P concentration after adjusting the phosphorus concentration was approximately 5.0 mg/L.

Table 1. Water quality of the treated water samples used for the experiments.

		Ave.	S.D.	Min.	Max.	n
pH		7.2	0.3	6.1	7.7	55
BOD	mg/L	5.0	2.8	<0.5	13	55
DOC	mgC/L	8.2	3.9	1.6	20	55
NH ₄ -N	mgN/L	1.8	2.2	<0.5	12	55
NO ₂ -N	mgN/L	0.25	0.19	<0.01	1.0	55
NO ₃ -N	mgN/L	6.8	4.1	1.5	21	55
Ca	mgCa/L	21.1	5.8	11	45	55
PO ₄ -P	mgP/L	5.0	0.2	4.5	5.7	55

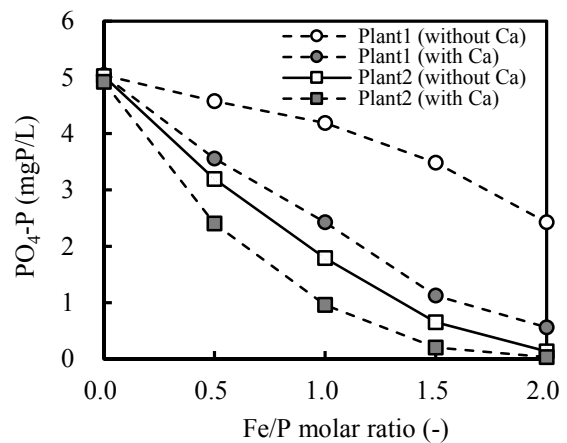


Figure 3. Phosphorus removal as a function of the Fe/P ratio without or with Ca addition.

The batch experiments were conducted using these treated water samples. Figure 3 shows the results obtained without and with Ca addition for two representative plants. With respect to plant 1

without the Ca addition, a tendency of decreasing PO₄-P was observed with the increase in the Fe/P molar ratio. However, even at a Fe/P molar ratio of 2, the PO₄-P was 2.4 mg/L, and therefore adequate phosphorus removal did not occur in this condition. In contrast, at Fe/P molar ratios of 1.5 and 2 in the case with Ca addition of 10 mg/L, PO₄-P concentrations were 1.1 and 0.56 mg/L, respectively. This indicated sufficient phosphorus removal took place in these conditions. These results were corresponding with the previous report in which the addition of iron by Fe/P molar ratio of 2.0 was enough to reduce phosphorus concentration below 1.0 (Rittmann and McCarty, 2001)

Improvement of phosphorus removal with Ca addition

A maximum difference of 2.4 mg/L was observed in PO₄-P when the cases without or with Ca addition were compared at a molar ratio of 1.5. Thus, it was revealed that phosphorus removal by the iron electrolysis method could be enhanced by Ca addition. Without Ca addition in plant 2, PO₄-P was lower at any molar ratio than that in the case with Ca addition in plant 1. Furthermore, in the case with Ca addition in plant 2, the PO₄-P concentration decreased further and PO₄-P was 1 mg/L even at a molar ratio of 1. Hence, it was suggested that the improvement in phosphorus removal by Ca addition using the iron electrolysis method was not constant. Moreover, Ca was present in the original sample as the Ca concentrations in plant 1 and plant 2 were 16 mg/L and 25 mg/L, respectively. Therefore, the differences in phosphorus removal could be owing to the sum of the initial and added Ca concentrations. As described above, the results of the experiments conducted on the actual treated samples obtained from the SWTPs confirmed that phosphorus removal was improved by Ca addition even in cases where the phosphorus removal performance deteriorated due to the poor Ca concentration.

Figure 4 shows the relationship between Ca and PO₄-P at molar ratios of 1 and 2 in the case without and with Ca addition. In the case without Ca addition at a molar ratio of 1, the PO₄-P varied largely in the range of 2.7 ± 0.90 mg/L and insufficient phosphorus removal was observed. These plots shifted to the lower right side in the case with the Ca addition of 10 mg/L, and the phosphorus removal stabilized in the range of PO₄-P 2.1 ± 0.63 mg/L. In the cases without and with Ca addition at a molar ratio of 2, the PO₄-P was stable in the ranges of 0.77 ± 0.79 mg/L and 0.32 ± 0.52 mg/L, respectively. The PO₄-P was equal to or less than 1.0 mg/L in 53 of the 55 samples with Ca addition at a molar ratio of 2. However, there was a case in which the PO₄-P was as high as 3.7 mg/L. The DOC was suggested as one of the factors that deteriorated the phosphorus removal since the DOC in the treated water was 20 mg/L in this sample. Figure 4 indicates that the Ca was considered to stabilize the phosphorus removal in the iron electrolysis method with a concentration of at least 20 mg/L.

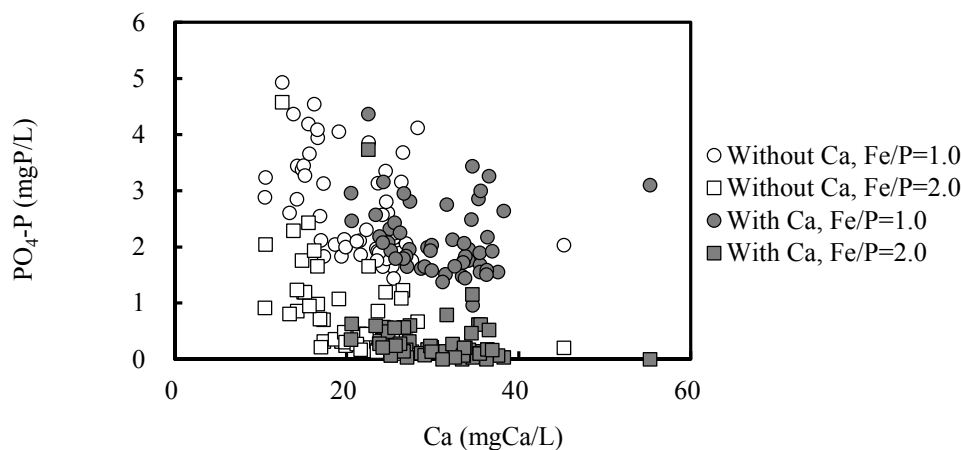


Figure 4. Relationship between Ca and PO₄-P for different Fe/P ratios.

Inhibition of phosphorus removal by DOC

Among samples without and with Ca at a molar ratio of 2, the 17 samples in which $\text{PO}_4\text{-P}$ did not decrease below 1.0 mg/L were selected. Figure 5 shows the relationship between the DOC and $\text{PO}_4\text{-P}$ in these samples. The $\text{PO}_4\text{-P}$ decreased with increasing molar ratios. However, the reduction in $\text{PO}_4\text{-P}$ with the molar ratio was not constant. In particular, a large decrease was obtained when the DOC was low. However, there was no substantial decrease even at a high molar ratio when the DOC was high. Therefore, it was clear that the DOC inhibited the phosphorus removal. This could be because the DOC in the wastewater includes components such as humic substance (Carstea et al., 2016). It was well known that iron produced the complex with the organics in lakes, (e.g. Nagai et al., 2007). It was also reported that the iron removal performance deteriorated in drinking water treatment process because it produced the complex with DOC (Knocke et al., 1992). Torrent et al., (1990) reported that the adsorption of phosphate on iron hydroxides had two phases, which was initially rapid phase and following slow phase. Wang et al., (2013) investigated the kinetics and adsorption-desorption properties of phosphate onto ferrihydrite, αFeOOH (goethite), and $\alpha\text{Fe}_2\text{O}_3$ (hematite). Gerke et al., (1993) reported that humic substances could initially inhibit P adsorption by poorly ordered Fe-oxide. Keeley et al., (2016) reported that the bound and solid Fe compounds were not available for phosphorus removal directly with precipitative mechanisms. Accordingly, the inhibition of phosphorus removal by the DOC could be considered as a consequence of the decrease in the quantity of iron combined with phosphorus due to the formation of complexes between the DOC and the iron supplied by the iron electrolysis method. Moreover, in the sample with DOC of 20 mg/L, additional experiments were performed by raising the amount of Fe/P molar ratio to 4. Consequently, the reduction of the $\text{PO}_4\text{-P}$ to less than 1 mg/L was found in this condition. It meant that the high amount of Fe/P molar ratio would be required in the high DOC conditions.

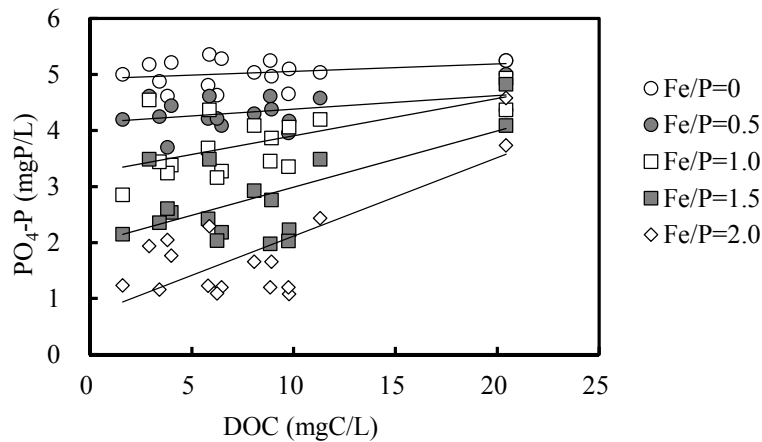


Figure 5. Relationship between DOC and $\text{PO}_4\text{-P}$ with poor phosphorus removal.

Table 2. The results of Pearson correlation analysis.

	$\text{PO}_4\text{-P}$	Fe/P molar ratio	Ca	BOD	DOC	pH	Alkalinity	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$
$\text{PO}_4\text{-P}$	1.000								
Fe/P molar ratio	-0.920 **	1.000							
Ca	-0.165 **	0.000	1.000						
BOD	-0.047	0.000	0.171 **	1.000					
DOC	0.038	0.000	0.066	0.519 **	1.000				
pH	-0.036	0.000	-0.159 **	0.014	-0.208 **	1.000			
Alkalinity	-0.071	0.000	0.172 **	0.308 **	0.340 **	0.362 **	1.000		
$\text{NH}_4\text{-N}$	0.025	0.000	-0.073	0.365 **	0.310 **	-0.141 **	0.376 **	1.000	
$\text{NO}_3\text{-N}$	0.018	0.000	0.228 **	0.000	-0.070	-0.610 **	-0.407 **	-0.150 **	1.000

Statistical analysis

Table 2 shows the results of the Pearson correlation analysis with PO₄-P, Fe/P molar ratio, Ca, and other water qualities. Since NO₂-N concentration was low compared to NH₄-N and NO₃-N, it was removed from this analysis. The maximum correlation coefficient between PO₄-P and Fe/P molar ratio was -0.920, and this was followed by -0.165 for Ca. Furthermore, no correlation was observed with respect to other water quality data including the DOC. Here, the absence of correlation between the DOC and PO₄-P was probably due to the fact that there were only few samples with high DOC concentration and the PO₄-P was reduced owing to high Ca concentration. These results indicated that notwithstanding an inhibition in the phosphorus removal achieved by the DOC, as a whole the PO₄-P could be controlled by the Fe/P molar ratio and Ca concentration.

The above results were considered, and multiple regression analysis was performed by selecting the PO₄-P as an object variable, and the Fe/P molar ratio, Ca, and DOC that affected the PO₄-P as dependent variables. Table 3 shows the results of the analysis. The adjusted R² was 0.875, and the p-values of all the variables were 0.001 or less. Therefore, the obtained model could express the experimental results well. The results indicated that the PO₄-P could decrease owing to an increase in Fe/P molar ratio and Ca, because the regression coefficients were negative for the Fe/P molar ratio and Ca. In addition, the regression coefficient of the DOC was positive, and thus the PO₄-P could increase with given increases in the DOC. According to the results of the analysis, PO₄-P decreased by 4.5 mg/L at a Fe/P molar ratio of 2, PO₄-P decreased by 0.8 mg/L with a Ca concentration of 20 mg/L, and PO₄-P increased by 0.2 mg/L with a DOC of 10 mg/L. Thus, the statistical analysis clarified the influence of coexisting substances such as Ca and DOC that affected the removal of phosphorus. Hence, based on these results, it was possible to estimate the amount of iron supplied from the iron electrolysis method that corresponded to the concentration of Ca or DOC.

Table 3. The results of multiple regression analysis.

Variable	Unstandardized coefficient	Standardized coefficient	t	P
Constant	5.67		50.5	<0.001
Fe/P molar ratio	-2.27	-0.920	-60.9	<0.001
Ca	-0.04	-0.168	-11.1	<0.001
DOC	0.02	0.049	3.22	0.001
R square: 0.875, Adjusted R square: 0.875, F: 1280, P: <0.001				

XAFS measurements

In the study, XAFS measurements targeting the produced particulate samples without or with Ca in plants 3 to 8 were performed to clarify the effect of Ca addition on the chemical state of iron. Figure 6 depicts the obtained XAFS spectra. The findings indicated that as a whole, no difference could be observed in the spectra obtained without and with Ca addition. Figure 6 also shows the R values expressing the fitting accuracy of the spectra without Ca relative to those with Ca. These values were obtained in the range of 0.008 % to 0.051 %. Mishima et al., (2016) examined the K absorption edge XAFS spectra of standard mixed iron samples. Their results indicated average R values of 0.031 % and a maximum of 0.069 % in the same synchrotron facility as that used in the present study. When compared with the R values obtained by previous studies, the R values obtained in this study were lower and both spectra corresponded with each other. Therefore, it could be concluded that there was no substantial change in the proportion of iron formed in the produced particulates by the Ca addition. According to Kaegi et al., (2010) and Voegelin et al., (2010), Fe

(III) particulates could form phosphorus containing flocks and were unlikely to grow to a size sufficient to flocculate sedimentation in the presence of phosphate ions and absence of Ca. The high phosphorus removal was observed due to more positive charge distributed on the solid surface with Ca^{2+} increasing (Li et al., 2013). It was also reported that the diameter of the spherical particles containing phosphorus and iron increased and larger spherical particles precipitated from Ca-containing than from Ca-free solutions (Kaegi et al., 2010). Moreover, Voegelin et al., (2010) reported that Ca uptake by Fe(III)–Ca-phosphate involved the linkage and coagulation of negatively charged Fe(III)-phosphate oligomers via Ca–O–P bonds in Ca-containing solution. Hence, the improvement of phosphorus removal by Ca addition combined with the iron electrolysis method was not considered as the consequence of the increased amount of FePO_4 , but was rather attributed to the accumulation of the coagulated particulate, which was insolubilized by the action of the positively charged Ca.

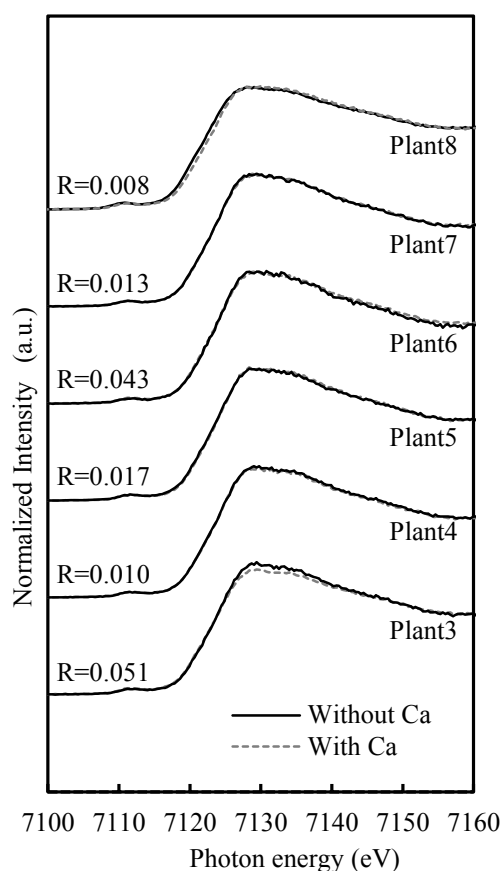


Figure 6. Comparison of XAFS spectra of produced particulates without and with Ca addition to the experiments.

CONCLUSION

In this study, laboratory-scale batch experiments via the iron electrolysis method were conducted to investigate the effect of phosphorus removal by using treated wastewater from small-scale wastewater treatment plants. The results indicated that the addition of Ca improved the phosphorus removal performance. Furthermore, phosphorus removal was inhibited in the presence of high DOC. The XAFS measurements of the produced particulates in the experiments showed no substantial change in the chemical state of iron without or with Ca addition. The statistical analyses revealed the range of improving or inhibiting effects on phosphorus removal owing to the Ca and DOC. Thus,

the results of this study provided useful information pertaining to the influence of coexisting substances on phosphorus removal and the chemical state of iron in the produced particulates in the iron electrolysis process.

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