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Treatment of Weak Sewage by Continuous Electrochemical Process using Noble Metal Electrodes

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In this study, both bench- and pilot-scale electrochemical processes adopting copper electrode were used for the treatment of weak sewage in small-scale communities. Considerable organics removal could be achieved during very shorter detention time of 2~3 minutes by continuous electrolysis procedure, and the nitrogen removal was mostly performed at the beginning of the electrolysis. Most phosphorus was also eliminated in the shorter detention time. It seemed that the phosphorus removal could be performed from the orthophosphate into copper hydrogen phosphate ($CuHPO_4$). The pH value also remarkably increased as electrolysis processed by higher concentration of hydroxyl ion through the electrolysis, whereas the pH value decreased to neutral ranges by additional aeration for 2 hours. In particular, total COD and total nitrogen were additionally decreased by aeration. The ORP value was gradually decreased with increasing detention time in both bench- and pilot-scale experiments. The ORP value considerably decreased in the pilot-scale experiment, which means the organics in the wastewater could be removed at more contiguous time and chance for wastewater during the electrolysis procedure.

Keywords: Electrochemical, Noble metal electrode, Weak sewage, Nutrient removal, Organics removal

1. INTRODUCTION

Sewage known as wastewater can create severe water pollution problems for aquatic life because of its various contents, and it has been mainly treated by aerated biological methods such as activated sludge process [1]. In general, conventional biological wastewater treatment has been primarily used to remove the colloidal or dissolved organic substances. However, considerable emphasis has been places on reducing the quantities of nutrients discharged, i.e., nitrogen and phosphorus, because they stimulate growth of algae and other photosynthetic aquatic life, which lead to accelerated eutrophication, excessive loss of oxygen resources, and undesirable changes in aquatic populations [2-4]. These limits can often be met with integrated process for nutrient control. Thus, many conventional biological treatment processes have been retrofitted for simultaneous removal of the nitrogen and phosphorus as well as the organics and solids in wastewater. Various flow schemes have been proposed and developed for the integration of carbon oxidation, nitrification, denitrification, and enhanced biological phosphorus removal [1, 2, 5].

The small-scale communities treating weak sewage should be effectively managed to remove nitrogen and phosphorus as well as organics with easy operation by a layperson with simple education. Also, it can counteract variable influent flux and quality with no limitation of seasonal variation. In general, the performance of biological nutrients removal process is strongly affected by the characteristics of the wastewater influent to each zone of the process. Neither biological nitrogen removal nor biological phosphorus removal can be also accomplished without sufficient biodegradable organic substrate as measured by BOD [2, 5, 6]. Therefore, application of biological nutrient removal processes in small-scale communities treating weak sewage with low influent concentration can cause serious problems such as lower removal efficiency and process stability due to system complexity.

The electrolysis process can be a candidate for the small-scale wastewater treatment because it is characterized by effective removal of pollutants by strong oxidation, easy operation by a layperson with simple education, no limitation by a seasonal variation, variable capability to variable influent flux and quality, rapid treatment, and mobile installation. A number of electrochemical processes have been derived to remove deleterious or dispensable constituents in water and wastewater, for example, electro-degradation [7, 8], electro-oxidation [9, 10], electro-flocculation [11], electro-coagulation [12-15], and so on. Most electrolysis processes use a couple of metallic electrodes. In usual, a relatively stable and a cathode such as titanium and a relatively active anode such as aluminum and iron were used. The redox potentials of aluminum and iron are -1.662V for $Al=Al^{3+}+3e^-$ and -0.440V for $Fe=Fe^{2+}+2e^-$, respectively. The more negative potential means the more active so that the electrode with the more negative potential can be easily oxidized. In case of copper, the redox potential is +0.337V for $Cu=Cu^{2+}+2e^-$, it means electrochemically noble [16].

The most important problem caused in electrolysis process for wastewater treatment is inconvenient management of electrode such as cleaning and replacement by a short service life. If the copper electrode is employed for the electrolysis process, the management of electrode can be more easily done. The other problem in the electrolysis process for wastewater treatment is discontinuous batch-type operation. In common, the reactor of electrolysis process is composed of batch-type tank and electrodes array. If the flow path in the process is being passed between the positive and negative electrodes during sufficient detention time, the process can be continuously operated. According to Chen [17], there are various designs for electro-coagulation, electro-flotation and electro-oxidation, which are mostly complicated to be difficult to manage the electrode such as cleaning and replacing. Thus, the composition of electrolysis reactor should be well organized for continuous operation and easy maintenance of electrodes.

Most electrolysis processes are operated under adjustable voltage and constant current conditions because of the treatment of high concentration non-degradable organic wastewater. However, existing technologies have limitations such as over-consuming of electric power with no consideration of the concentration of influent, complicated electrical authentication of facilities, and sudden dangers such as electric shock accidents [18]. In this study, an modified electro-chemical process was developed and the treatability of weak sewage in small-scale communities of a rural area was performed. The electrolysis reactor was improved with a new design, of which the electrode was made of copper and the process with continuous flow was operated under constant voltage and adjustable current conditions.

2. EXPERIMENTAL

In this study, both bench- and pilot-scale electrochemical processes were used for the treatment of weak sewage in small-scale communities, as illustrated in Figure 1(a) and Figure 2(b), respectively. Both electrochemical processes are comprised of three parts: electrolysis reactor, power supply, and cleaning system.

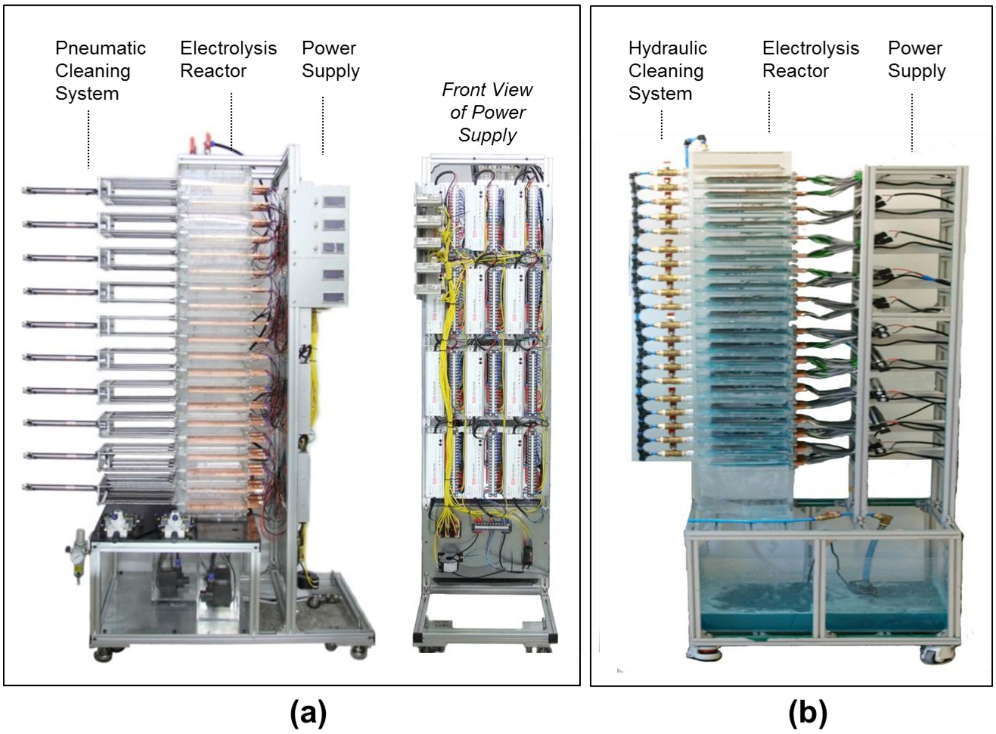

Figure 1. Schematic diagram of continuous electrolysis system

The electrolysis reactor consists of three trains, and the trains were installed in parallel for compact composition in the electrolysis reactor. Whereas the flow path in the reactor was in series being passed through each train. Each train was stacked as cassettes, of which modules were laminated with floors. Each floor had electrodes array which was composed of cathodes at the center part and anodes at both sides of the cathode.

The continuous electrolysis system was designed to adjust the current to the pollutant concentration at low bias voltage for energy saving and safety. The electrolysis experiment was performed under constant voltage of 24V and variable current with an upper limit of 10A. Overall, 12 power supply were used in the system and each power supplies supported variable currents directly under the voltage of 24V for one module. During the electrolysis procedure, the current value between the anode and cathode was measured simultaneously. The electrode cleaning equipment comprising continuous electrolysis system undertook a scraping with a brush for all cassettes. The specifications of both bench- and pilot-scale electrochemical processes are as shown in Table 1.

Table 1. Specifications of both bench- and pilot-scale electrochemical processes

	Bench-scale	Pilot-scale
Material of reactor	Plexiglass	
Total volume of train	2L	10.2L
Number of train in a reactor	3	1
Size of a train	40mmW×250mmL×1,200mmH	200mmW×250mmL×1,200mmH
Number of cassette in a train	4	10
Number of module in a cassette	5	2
Size of a module	40mmW×250mmL×50mmH	200mmW×250mmL×50mmH
Number of electrode in a module	3 (a cathode and two anodes)	21 (ten cathode and eleven anodes)
Size of an electrode	2mmW×190mmL×10mmH	
Electrode gap between the cathode and anode	7.5mm	
Material of electrode	Copper	
Type of electrode cleaning	Pneumatic	Hydraulic

Influent entering into the system was controlled by a fluid pump (IPX8/KSP-2500, G-Electronics), and introduced between the electrodes on the floor into the first train of the electrolysis reactor, which is defined as the primary treatment in this study. The primary effluent was also introduced subsequently in the second train, and then the secondary effluent treated in the second train was finally handled in the third train, denoted as the tertiary treatment. The detention time for each train was around 1.5 minutes and the flux was about 1.05L/min. In all steps, the wastewater was agitated to prevent the settling of by-products.

The sewage was collected directly from the end of the grit chamber in a wastewater treatment plant neighboring the amusement park located at Yeongwol in Korea. There were many restaurants and accommodations. The A^2O process, which was one of representative biological nutrient removal process, for advanced wastewater treatment with the capacity of 800m^3/d was operated. However, the influent fluctuation was very severe from 200 up to 500m^3/d due to the characteristics of amusement park.

The chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen (TN), and total phosphorus (TP) of the raw sewage ranged between 38~56 mg/L (average 50 mg/L), 5.5~16.5 mg/L (average 10.0 mg/L), 23.1~26.4 mg/L (average 24.8 mg/L), and 2.1~2.5 mg/L (average 2.2 mg/L), respectively. All analyses were conducted as per procedures in the American Public Health Association (APHA) Standard Methods [19]. Overall effluent was analyzed after settling for detailed observation of performance by electrolysis only. After the electrolysis of wastewater, aeration was performed to moderate the pH value which was increased by the electrolysis. To study the decomposition of organics in wastewater, Fourier transform infrared spectroscopy (FT-IR, Bruker optics, VERTEX80) analysis was performed. Also, the characteristics of sludge were analyzed by Field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700) and thermogravimetric analysis. Inductively coupled plasma emission spectroscopy (ICP-ES, Varian, 720-ES) was conducted to analyze a trace of metal ions in effluent and to confirm the metal composition of sludge.

3. RESULTS AND DISCUSSION

Figure 2 presents the photographs of influent wastewater and electrolyzed effluents with different detention times in the pilot-scale experiment. The color of influent wastewater was bright brown and that of electrolyzed effluents were bright blue with blue sludge, as shown in Figure 2. The sludge was accumulated by the increment of detention time in electrolysis process.

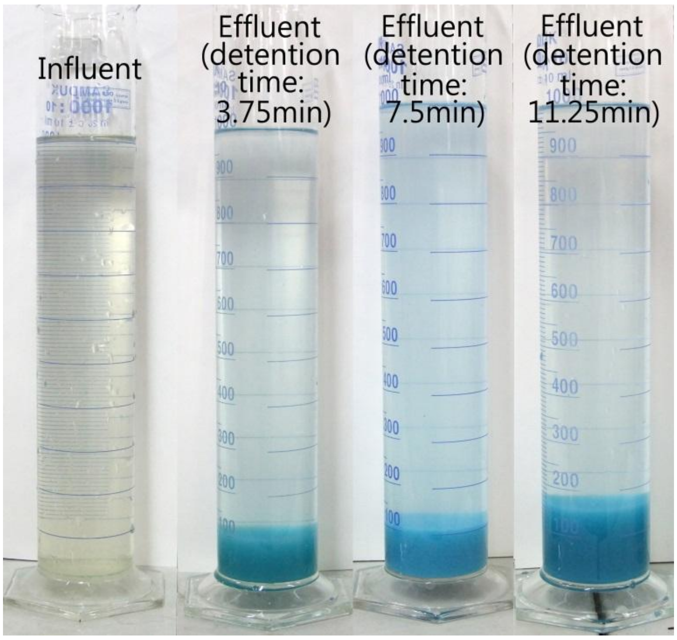

Figure 2. Photographs of influent and effluents (a)Influent wastewater and electrolyzed effluents before settling (b) Electrolyzed effluents after settling

Table 2 shows the result of inductively coupled plasma emission spectroscopy (ICP-ES) of influent wastewater and electrolyzed effluents to research metal ions. The higher concentration of Ca, K, Mg, Na, P, and Si were observed. The concentration of copper did not increase by the continuous electrolysis procedure, especially, and the phosphorus was considerably decreased.

Table 2. ICP result of influent wastewater and electrolyzed effluent (unit : ppm)

Sample	Influent	Effluent (detention: 3.75min)	Effluent (detention: 7.5min)	Effluent (detention: 11.25min)
Al	0.003	0.014	0.009	0.012
As	ND	ND	ND	ND
B	0.014	0.086	0.057	0.022
Ba	0.076	0.080	0.080	0.081
Ca	54.222	52.850	37.227	44.918
Cd	ND	ND	ND	ND
Cu	0.298	0.290	0.089	0.101
Fe	0.015	0.002	0.001	0.002
K	9.969	10.812	10.748	10.473
Li	0.002	0.001	0.001	0.001
Mg	10.371	9.884	9.148	8.537
Mn	0.008	0.003	ND	0.001
Mo	0.006	0.007	0.009	0.008
Na	20.840	20.841	21.001	20.330
Ni	0.002	0.002	0.002	0.001
P	2.357	0.074	0.021	0.042
Pb	ND	ND	ND	ND
S	1.474	1.084	1.063	1.044
Si	3.041	4.009	2.968	2.168
Sr	0.140	0.119	0.108	0.111
Zn	0.049	0.009	0.003	0.004

The electrolysis procedure generally accomplishes the decomposition of water into hydrogen at the cathode (reduction) and oxygen at the anode (oxidation) with an electric current being passed through the water [20]. In case of the electrolysis for wastewater, the various pollutants act as electrolytes, so that the electrical resistance could be lower than that of pure water.

The anion of pollutants in wastewater can form a compound with electrode metal at the anode during the electrolysis process. For example, the phosphate ion (PO_4^{-3}) can be copper phosphate ($Cu_3(PO_4)_2$). The phosphorus can be also oxidized at the anode with forming the phosphorus oxide (P_2O_5) and the copper can form the copper hydroxide ($Cu(OH)_2$). Such compounds, which is colored blue can be as revealed in Figure 2, are settled with the organics and other metal oxides in wastewater.

Figure 3 shows the changes of oxidation reduction potential (ORP) and conductivity in the bench- and pilot-scale processes. The values of ORP and conductivity in pilot-scale process were lower than those of bench-scale process over all because the contiguous time and chance for wastewater to contact with the electrode surface was more in pilot-scale experiment. The ORP was gradually decreased with increasing detention time in both cases. The ORP means whether the main reaction is oxidation or reduction in water and in general for biological wastewater treatment, the decrement of ORP value in the aerobic zone is regarded as the oxidation process of organics. It can be an indicator to recognize the decreasing current of organics although the decrement of ORP value is not quantitatively proportional to the oxidation rate of organics. Thus, the analysis of ORP variation behavior in a reactor is useful as basic data rapidly to counteract against the variable influent quality for the operation of wastewater treatment system [1, 21, 22]. As depicted in Figure 3, the ORP value considerably decreased in the pilot-scale experiment, which means the organics in the wastewater could be well removed at more contiguous time and chance for wastewater during the continuous electrolysis procedure. The conductivities in effluents were also decreased and the degree of decrement in the pilot-scale experiment was larger than that of the bench-scale experiment. The conductivity decrement can be explained by the loss of electrolyte ions in the effluents through the formation and agglomeration of compounds and then the sedimentation of solids. The aspects of conductivity variation were similar to the decrement of ORP value; the conductivity was more largely decreased in case of the pilot-scale experiment.

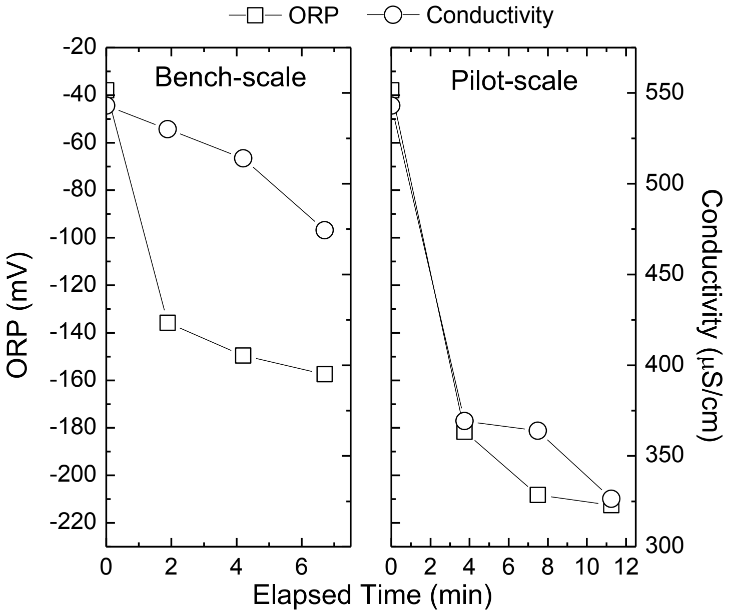

Figure 3. Changes of ORP and conductivity

The variations of chemical oxygen demands (COD) and biological oxygen demands (BOD) were presented in Figure 4. The concentrations of total COD and the soluble COD in influent were around 50mg/L and 30mg/L, respectively. The concentrations of total COD and soluble COD were dramatically decreased up to 10mg/L at the effluents in both cases, as shown in Figure 4(a). The concentration of total BOD was also about 15mg/L and very lower concentration of soluble BOD below 2mg/L was observed. The total BOD was removed up to below 1mg/L in both cases, as presented in Figure 4(b). Despite very shorter detention time of 2~3 minutes, especially, both COD and BOD were considerably decreased by electrolysis procedure.

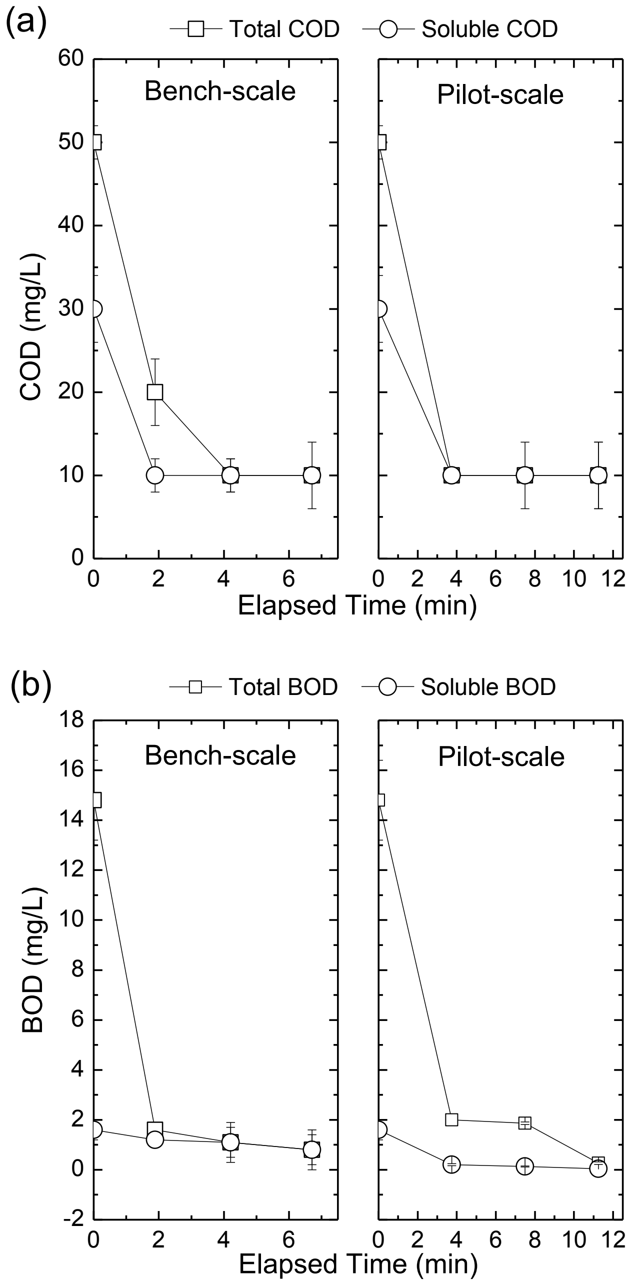

Figure 4. Changes of COD and BOD

Figure 5 presents the results of FT-IR analysis for influent and effluents in the pilot-scale experiment, for which the samples were prepared on the quartz glasses with the dried water drop. The influent wastewater involved the saturated hydrocarbon compounds with nitrogen. The compounds were very complicatedly mixed with the very broad peak, of which peak was difficult to index in detail. The compounds were changed by the continuous electrolysis of wastewater, as revealed in Figure 5.

The peak intensity of saturated hydrocarbon compounds of influent wastewater became lower, which means the compounds would be removed by the oxidation process at the anode.

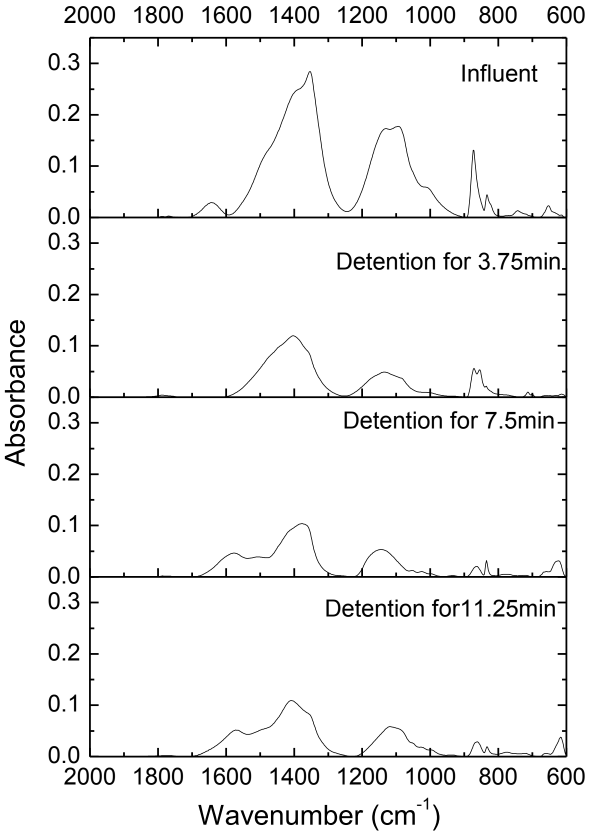

Figure 5. FT-IR of electrolyzed effluent

In general, the ammonia nitrogen (NH_4^+-N) is removed by the direct and indirect oxidation reaction during an electrolysis process; the direct oxidation reaction occurs at the anode and the indirect oxidation reaction takes place by oxides created during the electrolysis, respectively [23]. When the chloride ions (Cl^-) contained in the wastewater lose the electrons at the anode, chlorine gas (Cl_2) can be formed. Also, the chlorine gas is dissolved into water with the formation of hypochlorous acid (HOCl), proton (H^+), and chloride ion. The hypochlorous acid reacts with the ammonium ion (NH_4^+), consequently, the ammonium ion is stripped into the nitrogen gas (N_2). However, in this study, the concentration of NO_3^--N in influent was very high, while the ammonia nitrogen was relatively diluted. It was a matter to recirculation from the aerobic zone into the flow equalization tank of the wastewater treatment facility in the amusement park located at Yeongwol in Korea, at which the influent was sampled for this experiment.

Figure 6 presents the removal behavior of nitrogen with various detention times in the continuous electrolysis experiments. The nitrogen removal was mostly performed at the beginning of the continuous electrolysis and then the removal of nitrogen became slow. The removal rates of total nitrogen at the pilot-scale experiment as indicated in Figure 6 (b) were higher than the results of the bench-scale experiment as observed in Figure 6 (a). Especially, the concentration of total nitrogen was dominated by the removal of NO_3^--N, which was accomplished in an electrolysis process as follows [24];

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^-$$

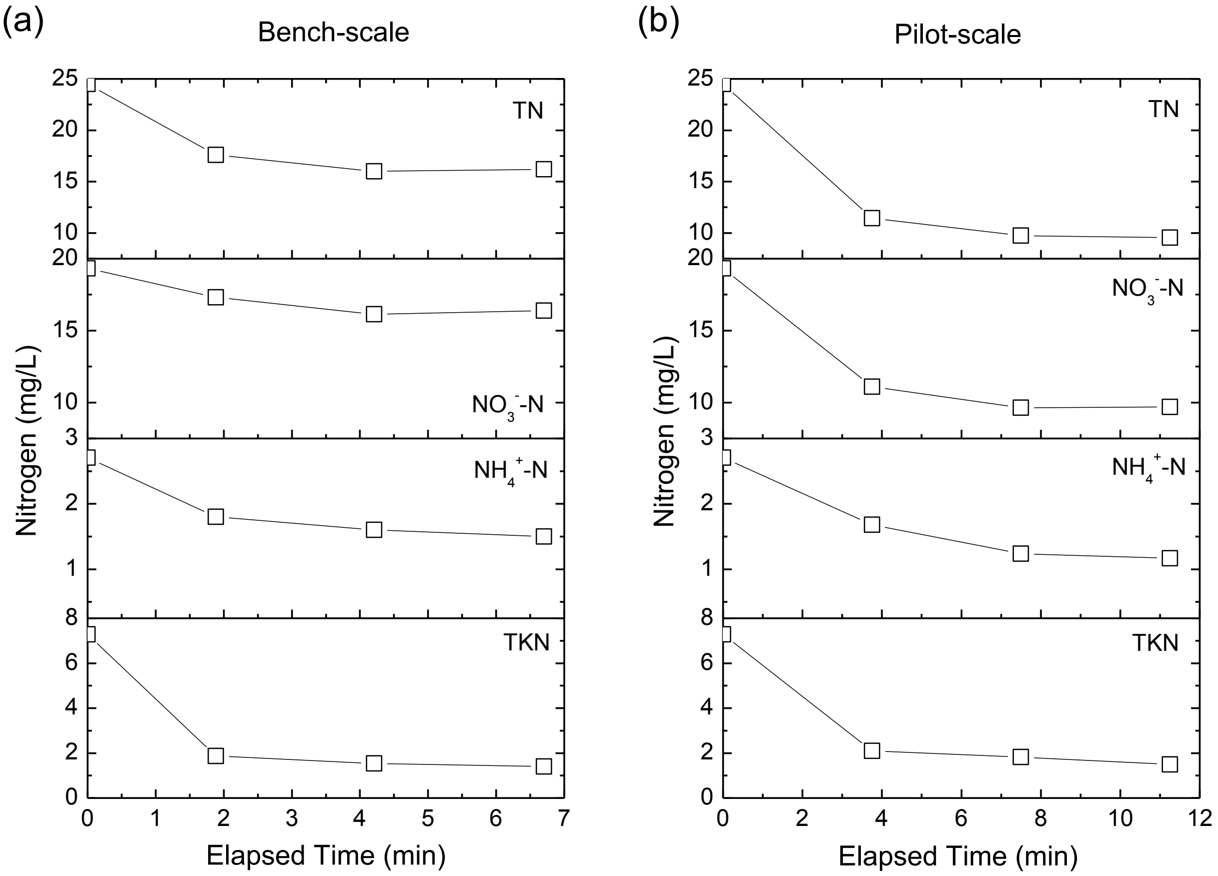

Figure 6. Effect of the electrolysis time on nitrogen removal

Figure 7 shows the removal results of phosphorus with increasing detention time in the continuous electrolysis experiments. Most of phosphorus was eliminated in the short detention time. The phosphorus removal mechanism could be explained as the followed equation;

$$3Cu(s) + 2PO_4^{-3} \rightarrow Cu_3(PO_4)_2(s) + 6e^-$$

$$3CuO(s) + 2PO_4^{-3} + 6H^+ \rightarrow Cu_3(PO_4)_2(s) + 6H_2O$$

$$3Cu(OH)_2(s)+2PO_4^{-3}+3H^+ \rightarrow Cu_3(PO_4)_2(s)+6H_2O$$

The phosphorus removal could be also performed from the orthophosphate into copper hydrogen phosphate ($CuHPO_4$) and then the phosphorus oxide (P_2O_5) might be formed with copper oxide (CuO) in the drying process of the sludge as follows;

$$Cu+HPO_4^{-2} \rightarrow CuHPO_4(s)$$

$$4CuHPO_4 \rightarrow P_4O_{10}(s)+4CuO(s)+2H_2O(g)$$

In the previous experiment [18], the phosphorus oxide (P_2O_5) was detected with very high intensity at the X-ray diffraction of the dried sludge as well as the copper phosphate ($Cu_3(PO_4)_2$) and copper phosphorus oxide (Cu_2PO_4). Consequently, the phosphorus could be removed rapidly by the formation of complicated compounds with metal during the electrolysis procedure.

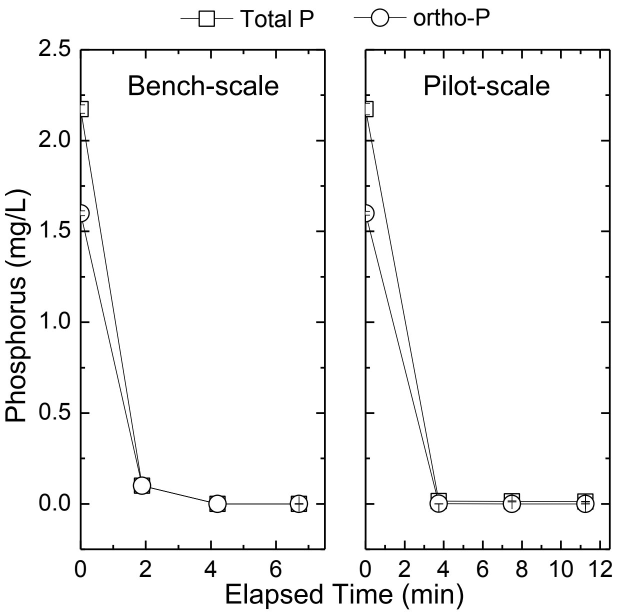

Figure 7. Effect of the electrolysis time on phosphorus removal

Figure 8 presents the variation of pH as electrolysis processed. As mentioned above, general electrolysis procedure results in the decomposition of water into oxygen at the anode and hydrogen at the cathode. If there are anions as electrolytes with less standard electrode potential than hydroxide, they will be oxidized instead of the hydroxide, and no oxygen gas will be formed. Also, if there is cations with a lower standard electrode potential than a hydrogen ion such as K^+, Ca^+, Na^+, and so on, the hydrogen gas will be produced [25]. In case of electrolysis for the wastewater, the hydrogen gas was produced at the cathode while no oxygen was produced, since there are lots of electrolytic ions with lower standard potential than hydroxide and hydrogen. Hence the concentration of hydroxide ion would be increased and the pH value could be raised, as presented in Figure 8. The change of pH value at the pilot-scale experiment was larger than that of the bench-scale experiment, because there were the longer detention time and more chance for wastewater to contact with the electrode surface in pilot-scale experiment. To reduce the pH value and to accomplish additional oxidation, an aeration process was performed after the continuous electrolysis. In bench-scale experiment, the pH value decreased from 9.66 to 8.22 by the aeration for 2 hours. It was also reduced from 10.42 to 8.09 by the same aeration process in pilot-scale experiment. In particular, total COD and total nitrogen were additionally removed by aeration from 10mg/L to 0mg/L and 9.5mg/L to 8.7mg/L for 2 hours, respectively.

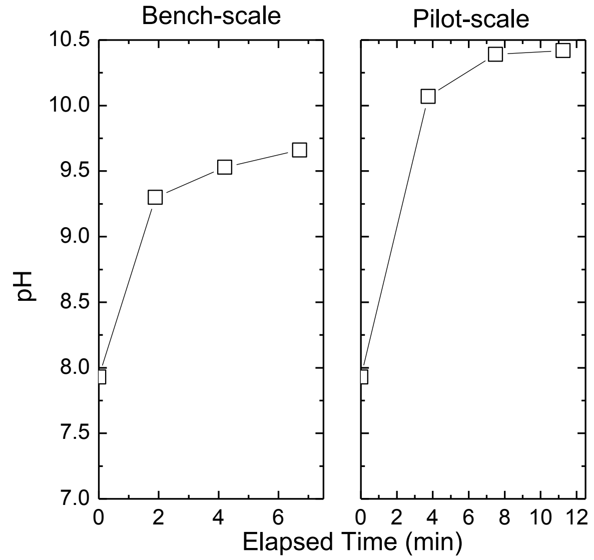

Figure 8. Variation of pH value by electrolysis time

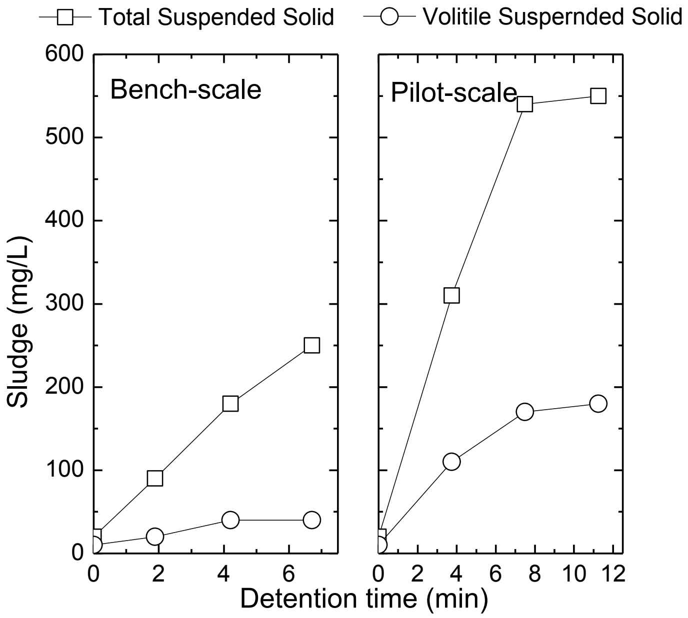

Figure 9. Produced sludge after the electrolysis time

Figure 9 shows the produced sludge by the electrolysis procedure. The pilot-scale experiment induced more sludge than that of bench-scale results because of the higher removal efficiencies. In synthetically consideration with above results, the detention time of less than 4 minutes was enough to remove the pollutants in the wastewater and more electrolysis was needless. To remove the pollutants of around 60mg/L including COD, TN and TP, the sludge of about 300mg/L was produced. Relatively large amount of sludge was on account of inorganic compounds containing copper of high specific gravity.

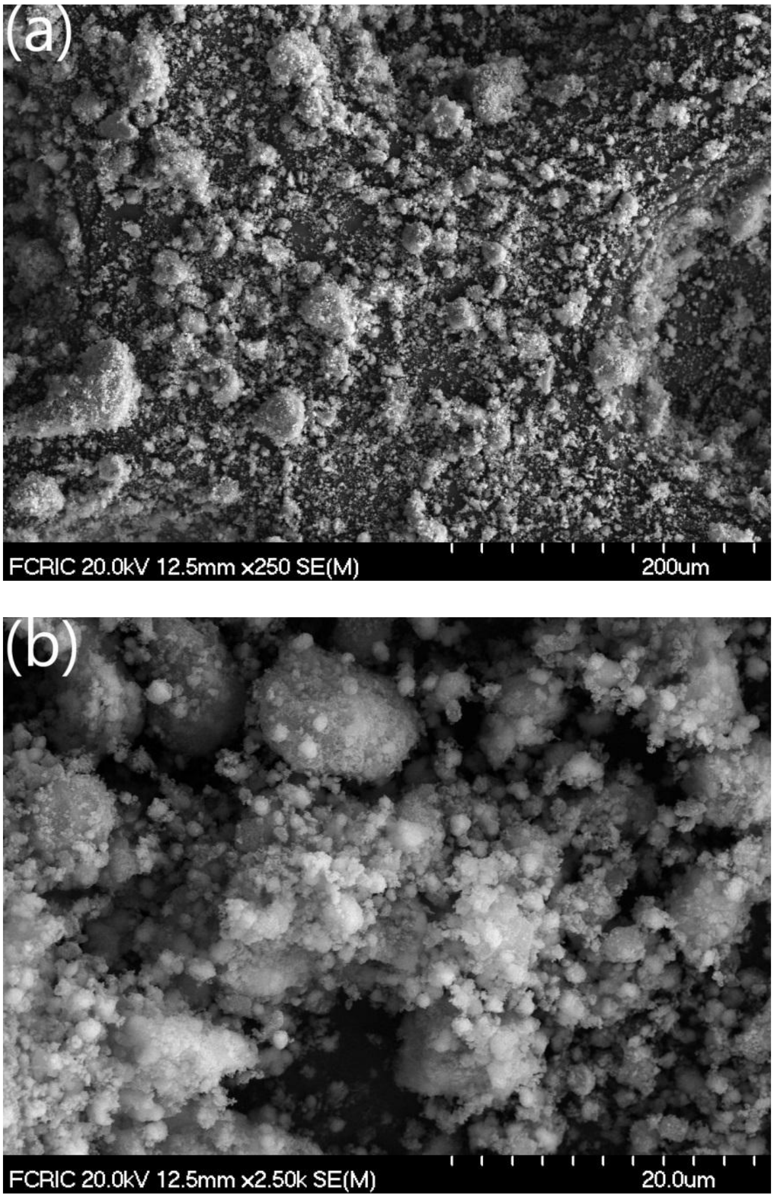

Figure 10. SEM of sludge from tertiary effluent

The microstructure of the dried sludge observed by FE-SEM was presented in Figure 10. As shown in Figure 10(a), the sludge was composed of lots of powder-like agglomerates of which size was from several micrometers to several ten micrometers. In high magnified observation as revealed in Figure 10(b), the sludge were consisted of very small primary particles and several micrometers agglomerates by the primary particles were aggregated to form several tens micrometers particles agglomerates. The continuous electrolysis process removed the various pollutants in the wastewater and in the meanwhile the complicated copper compounds were formed as particles with the pollutants. When the inorganic particles were aggregated each other, the organics could be accompanied in the agglomerates.

Figure 11 shows the results from TGA of the dried sludge. Increasing the temperature, the weight of sludge considerably decreased up to around 300°C and then slowly reduced up to about 600°C. The sludge produced at the initial stage of the continuous electrolysis process for 3.75 minutes included the organics of 60 weight percent, which was revealed by weight loss. Increasing the detention time, the weight loss became less up to 40 percent. It means that most of pollutants including the organics would be removed at the initial stage of the continuous electrolysis process.

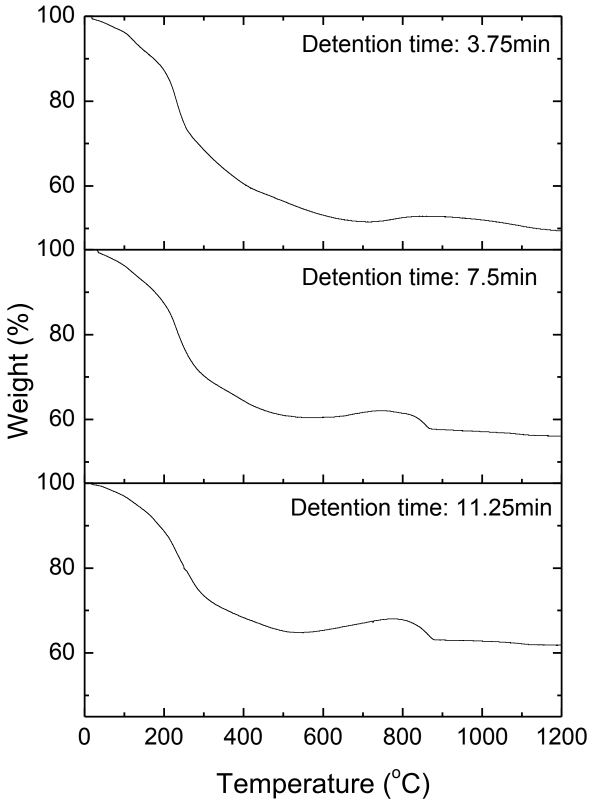

Figure 11. TGA of sludge

The ingredients in the sludge were investigated as presented in Table 3. The representative ingredients in the sludge were Ca, Cu, Mg, and P. Water usually contains calcium and magnesium as shown in Table 2. They could be oxidized during the electrolysis. Phosphorus removed from the wastewater by the formation of the complicated compounds with copper and then included into the sludge. As mentioned above, the major components of sludge were copper, which might be recycled as resources of copper.

Table 3. ICP result of sludge (wt.%)

Sample	Sludge (detention: 3.75min)	Sludge (detention: 7.5min)	Sludge (detention: 11.25min)
Al	0.369	0.217	0.179
Ca	5.754	5.917	4.270
Cu	86.077	88.264	91.164
Fe	0.325	0.159	0.127
K	0.524	0.613	0.307
Mg	1.372	0.815	0.863
Na	0.694	0.745	0.413
P	3.998	2.280	1.855
Zn	0.676	0.646	0.667

4. CONCLUSION

In this study, both bench- and pilot-scale electrochemical processes were used for the treatment of weak sewage in small-scale communities. The modified electrolysis processes were applied adopting copper electrode, continuous flow, and operation under constant voltage and adjustable current. The ORP value was gradually decreased with increasing detention time in both bench- and pilot-scale experiments. The ORP value considerably decreased in the pilot-scale experiment, which means the organics in the wastewater could be well removed at more contiguous time and chance for wastewater during the continuous electrolysis procedure.

The organics such as COD and BOD were removed considerably during very shorter detention time of 2~3 minutes as the electrolysis was processed. The concentrations of total COD and soluble COD were dramatically decreased up to 10mg/L guaranteeing the effluent criteria of wastewater treatment. The nitrogen removal was mostly performed at the beginning of the continuous electrolysis, and the removal rate of total nitrogen at the pilot-scale experiment was higher than the results of the bench-scale experiment. Most phosphorus was also remarkably eliminated in shorter detention time. It seemed that the phosphorus removal could be performed from the orthophosphate into copper hydrogen phosphate ($CuHPO_4$). The pH value also remarkably increased as electrolysis processed by higher concentration of hydroxyl ion through the electrolysis, whereas the pH value decreased to neutral ranges by additional aeration for 2 hours. In particular, total COD and total nitrogen were additionally decreased by aeration from 10mg/L to 0mg/L and 9.5mg/L to 8.7mg/L, respectively.

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