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Application and Assessment of Enhanced Electrolytic Process for Laundry Wastewater Treatment

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In this research, an enhanced electrolytic process was applied and evaluated for the treatment of laundry wastewater. Treatability of the process as well as the analyses of by-product was also conducted. Most organics in laundry wastewater were formed of suspended solids and they were removed successfully by electro-coagulation mechanism. The TKN was removed completely in a very shorter retention time of three minutes; in particular, the removal of overall phosphorus was performed in only 1.4 minutes. The pH value increased whereas alkalinity decreased due to the carbonates eliminated during the electrochemical procedure. The ORP value declined because the copper electrode has oxidation-reduction half potential of -0.15V during being oxidized Cu to Cu^{2+}. The sludge was by-product of the procedure, and its SVI was below 20mL/g. The sludge had a good settleability and it would be easy to liquid-solids separation. The aeration after electrolytic procedure was performed for two hours and it was sufficient solution for additional removal of organics and neutralization of pH value.

Keywords: Electrolytic process, Copper Electrode, Laundry Wastewater, Wastewater Treatment

1. INTRODUCTION

Laundry wastewater is a major component of domestic sewage in Korea, accounting for about 25% of total discharge [1]. The important constituents of concern in laundry wastewater are many contaminants from laundries and the chemicals such as detergents and surfactants, which are very slow to degrade. It causes foaming problems and produces adverse effects on the beneficial use of natural water and sewage treatment plant operation. Higher concentrations of suspended solids (SS) and biochemical oxygen demand (BOD), the levels of oil and grease, and nutrients such as nitrogen and phosphorus exceed municipal wastewater discharge standards, if untreated laundry wastewater containing many contaminants and chemicals is discharged. It can also lead to accelerate eutrophication and excessive loss of oxygen resources [2-4]. Eutrophication can be prohibited by the control of either nitrogen or phosphorus [5, 6]. Thus, the importance of the laundry wastewater treatment has been increasingly recognized.

In general, biological activated sludge process [7] is the most commonly used for the treatment of laundry wastewater. However, the biological activated sludge process has severe limitations of the performance and reliability due to the sensitivities by environmental parameters and operating complications. In recent years, to overcome the problems of biological laundry wastewater treatment, many researches such as membrane filtration [3], advanced oxidation process (AOP), and electrochemical treatment [3, 7, 8] are conducted.

The electrochemical methods for the treatment of laundry wastewater were started from the developed countries. The electrochemical treatment can be defined the technology for the removal of pollutants in wastewater by electrolysis [8-10] and electro-coagulation [11-13]. The electrolysis is the representative treatment method of wastewater, which contains both organic and inorganic electrolytes, by direct oxidation on the anodes or indirect oxidation using by-products such as hypochlorous acid (HOCl). The electro-coagulation is another technique for the removal of the pollutants in sewage by separating coagulated and flocculated contaminants with eluted ion from electrodes, using sedimentation or floatation by hydrogen and chlorine gas. Lately, the electrochemical treatment is applied to many kinds of wastewater from oil pollution [15, 16], bilge [15], textile [15, 17], paper industry [12, 18], and swine [19]. A number of researches on the laundry wastewater treatment have been also performed, for example, electrochemical degradation of surfactants [7], electro-coagulation [8, 20, 21], and so on.

The performance of electrochemical treatment can be severely affected by the current, voltage, retention time, and the kinds of electrodes due to the using of electricity as the energy source for the reaction. The performance of electrolysis also increases, as the current increases during the electrolysis procedure, but the energy efficiency decreases [22, 23]. The removal efficiency would be improved under the condition of higher voltage, whereas the loss of electronic power occurs in that case [24, 25]. The electrolysis performance can be also improved by the longer retention time, in spite of that, the retention time of longer than 30 minutes rarely have an effect on the treatability [8, 12, 21]. Ozyonar and Karagozoglu [26] reported that the optimum retention time for the treatment of municipal wastewater by EC process was 5 to 10 minutes.

The specific energy consumption increases generally in proportion to the retention time, voltage, and current, as follows;

$$SEC = 10^{-3} J \cdot U \cdot t \quad (1)$$

where, SEC is the specific energy consumption (kWh/m^3); J is the total current applied (A); U is the overall cell voltage (V); t is the time needed for the removal of a given pollutant (h).

In common, Ohm's law states that the current through a conductor between two points is directly proportional to the voltage across the two points. In this research, the process was operated under constant voltage and adjustable current conditions to overcome the disadvantages of existing electrolysis technologies such as complicated electrical authentication of facilities, over-consuming of electric power with no consideration of the concentration of influent, and dangers by electric shock injury accidents. As the voltage is constant, therefore, the resistance causing by the water quality of influent can be affected by the current. A couple of metallic electrodes, usually a relatively stable cathode such as titanium and a relatively active anode such as aluminum and iron, were used in most electrochemical treatments [27]. However, the copper electrodes have many advantages such as easier maintenance and higher performance than aluminum or iron electrodes [28].

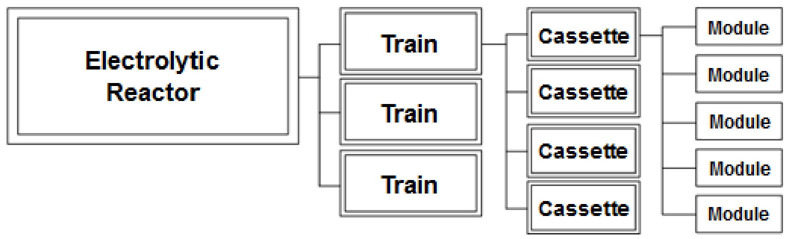
We have conducted the present research in order to evaluate the treatability of organics and nutrients in the laundry wastewater by using electrochemical treatment process with copper electrodes under adjustable current and constant voltage. The analyses of sludge production and characteristics were also conducted in detail.

2. EXPERIMENTAL

Most existing electrolysis technologies are operated generally in a fed-batch manner. As shown in Figure 1, however, the enhanced laboratory-scale continuous flow electrochemical treatment process was devised and applied for the treatment of laundry wastewater. Mainly, this process consisted of three parts: electrochemical treatment reactor which made of plexiglass, power supply, and pneumatic cleaning instrument. The electrochemical reactor was composed of three trains, and the one train was made up of four cassettes. Each module was equipped with three copper electrodes. The centered electrode was cathode and the two electrodes of sides were anodes, for improving performance of electrochemical treatment.

The electrochemical treatment process was operated under adjustable current and constant voltage, because flowrate and water quality can have effects on the performance of process. The electrolysis experiment was carried out under variable current with an upper limit of 10A and constant voltage of 24V. 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. The pneumatic cleaning instrument, which was driven by pressure of nitrogen, gas removed the attached scale on the electrodes and settled sludge in the modules.

(a)



(b)

Parts	W (mm) x L (mm) x H (mm)	Notes
Train	40 x 250 x 1,200	4 Cassettes consisted of 1 Train.
Cassette	40 x 250 x 250	5 Modules consisted of 1 Cassette.
Module	40 x 250 x 50	3 electrodes equipped in 1 Module.
electrode	2 x 190 x 10	Copper. 1 cathode between 2 anodes.

(c)

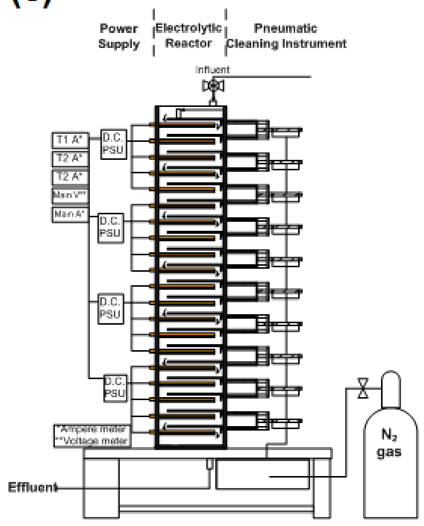


Figure 1. (a) Structure diagram of continuous electrochemical treatment process (b) Specifications of electrochemical treatment process parts (c) Schematic diagram of continuous electrochemical treatment process

The flowrate of 1.45L/min and the retention time of 1.3min, respectively, were applied in the process. The final effluents were recirculated to evaluate the influence of retention time. Laundry wastewater, as the influent, was supplied into the reactor by fluid pumps (IPX8, KSP-2500). The effluent tanks for sampling were installed under the each train and the samples used after sedimentation.

The laundry wastewater was collected from the laundry plant located at Jeongseon in Korea. The laundry plant mainly treated beddings of hotels. The pH, alkalinity, and ORP (Oxidation-Reduction Potential) of the laundry wastewater ranged between 7.2~9.4 (average 8.3), 150~155 mg/L (average 152 mg/L) and -155~-24 mV (-89 mV), respectively. The total solids (TS) and volatile solids (VS) were also 340~540 mg/L (average 440 mg/L) and 235~400 mg/L (average 320 mg/L), respectively. As shown in Table 1, the concentrations of organics such as COD (Chemical Oxygen Demand) and BOD (Biochemical Oxygen Demand), and nutrients such as nitrogen and phosphorus were summarized, respectively.

Table 1. Concentrations of organics and nutrients in laundry wastewater [Unit : mg/L, minimum~maximun (average)]

Organics				Nutrients		
COD		BOD		Nitrogen		Total Phosphorus
Total	Soluble	Total	Soluble	TKN*	Nitrate	
210~340 (275)	100~110 (105)	23~25 (24)	23~25 (24)	3.2~8.9 (5.5)	5.9~8.4 (7.1)	0.1~0.6 (0.4)

*TKN : total Kjeldahl nitrogen (Sum of organic nitrogen and ammonium)

All analyses were conducted as per procedures in the American Public Health Association (APHA) Standard Methods [29]. Samples were used the supernatants of effluents after sedimentation during 30 minutes to evaluate the removal characteristics of electrochemical treatment. The metal impurities in treated effluent were determined by inductively coupled plasma emission spectroscopy (ICP-ES, Varian 720-ES). The residual organics in the treated effluent were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Bruker optics, VERTEX80). After the electrolysis experiment, the microstructure and thermal characteristics of the by-products, i.e. the sludge, were also examined by field emission scanning electron microscopy (FE-SEM, HITACHI, S-4700) and thermogravimetric analysis (TGA, SHIMADZU, DTG-60H).

3. RESULTS AND DISCUSSION

The electrochemical treatment process which used copper electrodes was treated laundry wastewater under the conditions of adjustable current and constant voltage in this study. During the shorter retention time below 6 minutes, the COD removal of 72.7%, the TN removal of 41.2%, the TP removal of 95% could be achieved, respectively. The current also decreased 0.51A to 0.38A through the removal procedure of pollutants in laundry wastewater.

3.1. Organics removal

In electrochemical treatment, the organics are removed generally through both electrolytic oxidation and electro-coagulation. The procedures of electrolytic oxidation and electro-coagulation can be expressed as follows;

[Reaction of electrolytic oxidation]

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (2)$$
$$OH \rightarrow 2H_2O + O_2 + 4e^- \quad (3)$$
$$\text{organics} + O_2 \rightarrow H_2O + CO_2 \quad (4)$$

[Reaction of electro-coagulation]

$$H_2O \rightarrow 1/2\ H_2 + OH^- \quad (5)$$
$$\text{Metal} + nOH^- + \text{Organics} + O_2 \rightarrow \text{Oxidized Organics-Metal(OH)n}\downarrow + ne^- \quad (6)$$
$$2H_2 + 2e^- \rightarrow H_2\,(g) \quad (7)$$

Figure 2 illustrates the behavior of organics in the laundry wastewater during the procedure of electrochemical reaction. Most TCOD (Total COD) containing suspended organics was successfully removed at the beginning of the electrochemical reaction. Although the reaction time was extended, however, lower removal of soluble COD which represents the dissolved organics was observed. It should be noted that most organics removal in this process could be achieved by the electro-coagulation. This result was equal to that of Reyter *et al.* [9] investigated the relationship of removals between turbid matter and organics removal.

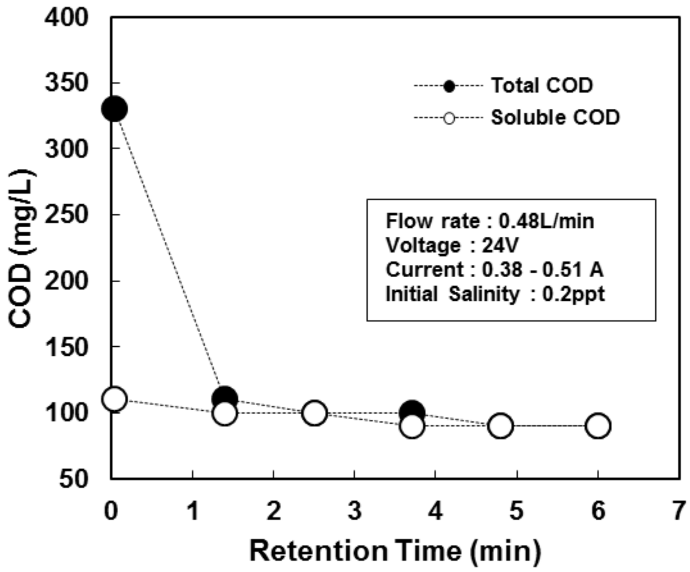


Figure 2. Organics removal characteristics of laundry wastewater by electrochemical treatment

The removal of soluble organics by electrochemical treatment process can be deteriorated due to some causal effect such as lower concentration of salinity in wastewater, relatively short supply of electric power by using of low voltage, and insufficient retention time for electrochemical reaction. In general, the concentration of salinity in the water is related with the organics removal. The salinity is a parameter to indicate the concentration of electrolytes. When the higher concentration of salinity in the water is dissolved, therefore, the current increases and the organics removal will be improved. There are researches supplying the electrolytes such as sodium chloride, chlorine, or chloride to improve organics removal [22, 30-32].

In this research, as mentioned above, the conditions of constant voltage and adjustable current were applied to the process unlike conventional electrochemical treatment. The electric power is multiplying current by voltage, and the electric power of 9.12 watt to 12.24 was observed. In a number of researches, electric power above 50 watt was applied in electrochemical treatment, and higher organics removal could be achieved [11, 20, 33, 34]. In this study, the result of lower organics removal is also likely to react insufficiently unlike other researches suggesting the retention time above 15 minutes [11, 17, 18, 20, 32, 33]. Surface active agent is one of major soluble organics in the laundry wastewater. Its removal can be improved by using boron-doped diamond thin film electrodes which have high oxidizing power or supplying salts [8, 9, 22, 32]. Aeration after electrochemical procedure would be another solution for the additional organics removal. In this study, the examination for additional organics removal by aeration was carried out after the electrochemical treatment, and its result was shown in Figure 10.

3.2. Nitrogen removal

As shown in Figure 3, the total nitrogen could be removed through the electrochemical reaction, and this appeared by the elimination of total Kjeldahl nitrogen (TKN).

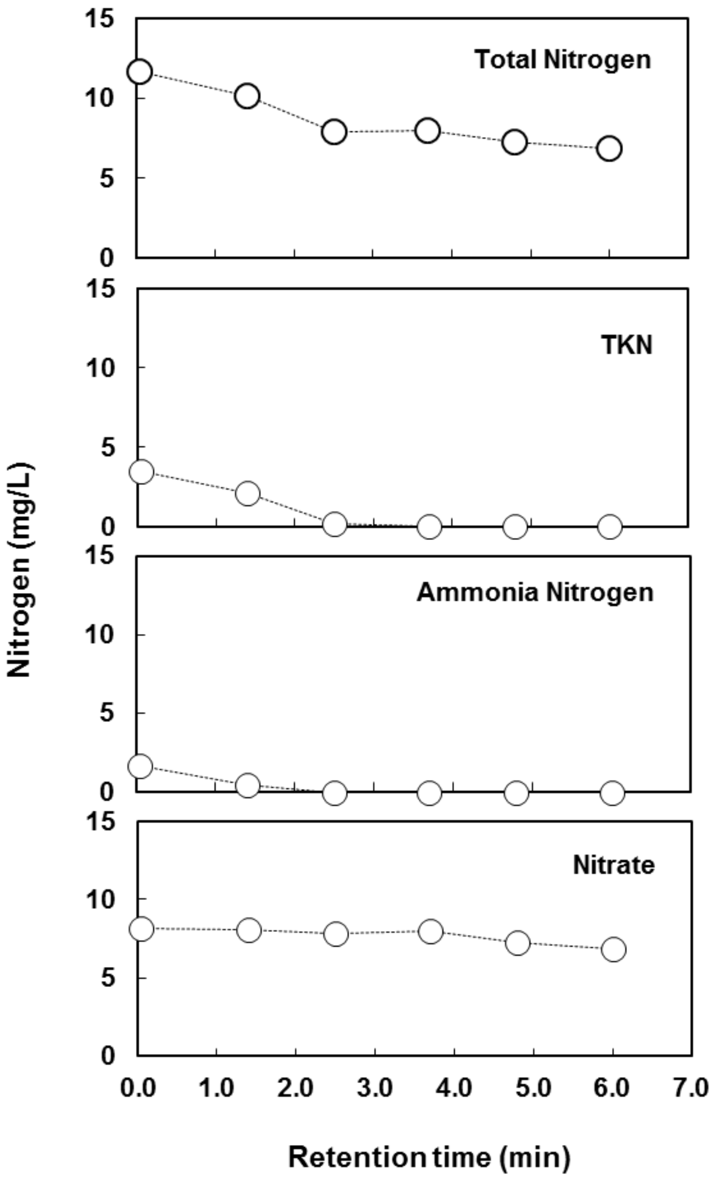


Figure 3. Nitrogen removal characteristics of laundry wastewater by electrochemical treatment

The ammonia nitrogen which consists of TKN was removed in a shorter retention time below two minutes. Generally, the removal of ammonia nitrogen by electrolysis includes the direct and indirect oxidation reactions [35]. The direct oxidation reaction of ammonia nitrogen occurs at the anode and the indirect oxidation reaction also takes place through oxides created during the electrolysis [36]. The concentration of organic nitrogen, TKN except ammonium, decreased after the ammonia nitrogen removal. The mechanism of ammonium nitrogen removal is suggested as follows;

$$2NH_4^+ + 3HOCl \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \qquad (8)$$

Most organic nitrogen exist a form of solid. And then it could be removed through the mechanism of electro-coagulation, as mentioned above in the Equation (5) to (7). The nitrate was removed slightly despite the increasing of retention time. The reaction of nitrate removal by electrochemical treatment can be expressed as follows;

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

or

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (10)$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \qquad (11)$$

However, some of nitrate would be formed by the reaction between the hypochlorous acid and the ammonium ion as follows;

$$0.25NH_4^+ + HOCl \rightarrow 0.25NO_3^- + 0.25H_2O + 1.5H_+ + Cl^- \qquad (12)$$

In our previous research [36], actually, the concentration of nitrate slightly increased. The study of Cho *et al.* [19] also had results that nitrate concentration increased or had no change depending on salt level. The incomplete nitrate removal was observed, whereas the concentration of total nitrogen after electrochemical reaction guaranteed the effluent standard of wastewater treatment plant (WWTP) in Korea.

3.3. Phosphorus removal

Generally, eutrophication can be prevented by the control of either nitrogen or phosphorus. Because the concentration of phosphorus is usually lower than that of nitrogen in wastewater, phosphorus removal may be more effective than that of nitrogen from ecological and economical points of view. Figure 4 shows the removal of phosphorus in laundry wastewater by the electrochemical treatment, and excellent phosphorus removal could be achieved during shorter retention time within two minutes.

The electrochemical treatment is a very useful method to remove just about any pollutant, especially phosphate, in water and wastewater. Higher removal of phosphorus can be achieved by electrochemical reaction as same as other studies [14, 37], the removal was performed through the formation of copper phosphate ($Cu_3(PO_4)_2$) at the anode in this study. The phosphorus removal reaction by electrochemical method can be expressed as follows;

$$Cu_{(s)} + 2H_2O \rightarrow Cu^{2+}(aq) + 4H^+ + O_2 + 4e^- \quad (13)$$
$$Cu^{2+} + PO_4^{3-} \rightarrow Cu_3(PO_4)_{2(s)} \downarrow \quad (14)$$
$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_{2(s)} \downarrow \quad (15)$$

Thus, it was believed that the modified electrochemical treatment process using copper electrode devised in this study could be a good candidate of existing phosphorus removal process, and it could be contributed to the control of eutrophication.

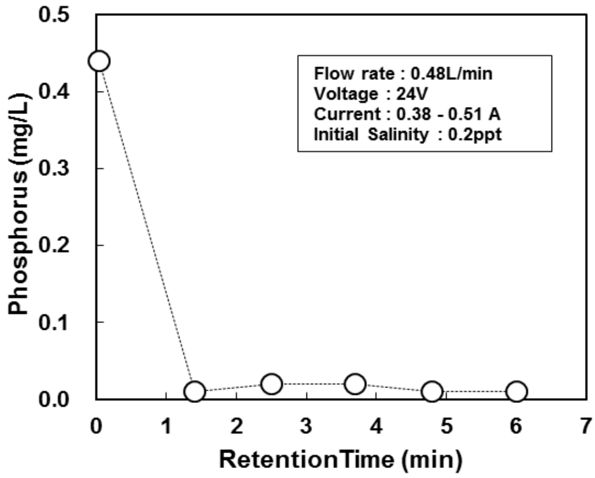


Figure 4. Phosphorus removal characteristics of laundry wastewater by electrochemical treatment

3.4 Changes of pH and alkalinity

As noted above in Equation (5), hydroxyl ion (OH^-) is generated from decomposition of water by electrochemical treatment. The pH of water increases because of OH^- generated. Figure 5 illustrates the changes of pH and alkalinity depending on the retention time.

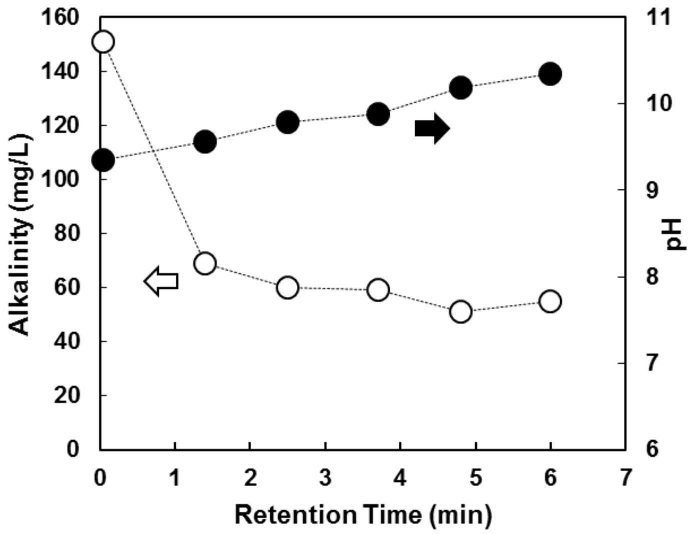


Figure 5. Changes of pH and alkalinity in electrochemical treatment of laundry wastewater

The increment of pH value was observed after electrochemical decomposition of pollutants in wastewater, whereas the alkalinity decreased through the electrochemical reaction. The induction substances of alkalinity in water or wastewater are OH^-, carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-), respectively. The CO_3^{2-} or HCO_3^- was removed by electro-coagulation during electrochemical reaction time, and it could be explained from the similarity between decrement of the alkalinity and total COD.

3.5 Changes of ORP and conductivity

Oxidation-reduction potential (ORP) and conductivity are the indicators to check electrochemical state of water. Oxidation-reduction half potential of copper is -0.15V when Cu oxidizes to Cu^{2+} [38, 39]. The copper electrodes dissolved in the water during processing treatment, and it led to decreasing of ORP. Increasing pH also has an effect on decreasing ORP, but its influence would be small as known.

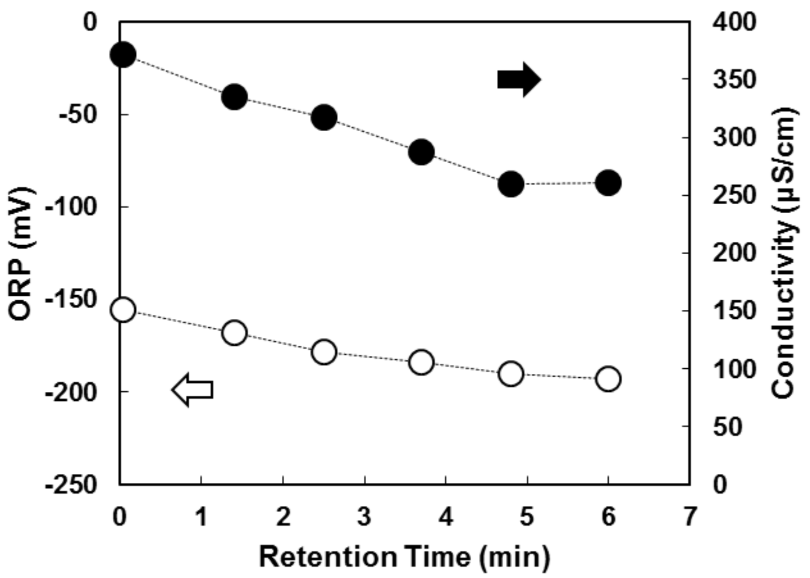


Figure 6. Changes of ORP and conductivity in electrochemical treatment of laundry wastewater

Conductivity also decreased during electrochemical treatment of laundry wastewater. Several kinds of ion can be by-products such as sludge with Cu^{2+} and it leads to decrease the conductivity. Removal of organics and nutrients declined after retention time of three minutes, whereas the mass produce of sludge increased because the copper oxides ($Cu(OH)_2$) was formed during electrochemical procedure.

3.6 Sludge characteristics

Sludge which contains pollutants or eluted electrode is produced in electrochemical treatment process. The final effluent of the process should be discharged after liquid-solids separation, thus the settling chracteristics of sludge can be one of important parameters in the process. Two commonly used measures developed to quantify the settling characteristics of sludge are settled volume of sludge after 30 minutes (SV_{30}) and sludge volume index (SVI). SV_{30} determined by placing a sample in a one to two liters cylinder and measuring the settled volume after 30 minutes. SVI is the SV_{30} corresponding suspended solid (SS) concentration of sample. As SV_{30} and SVI are lower, the settleability of sludge is better. The SV_{30} and SVI of sludge which produced by electrochemical treatment were illustrated in Figure 7.

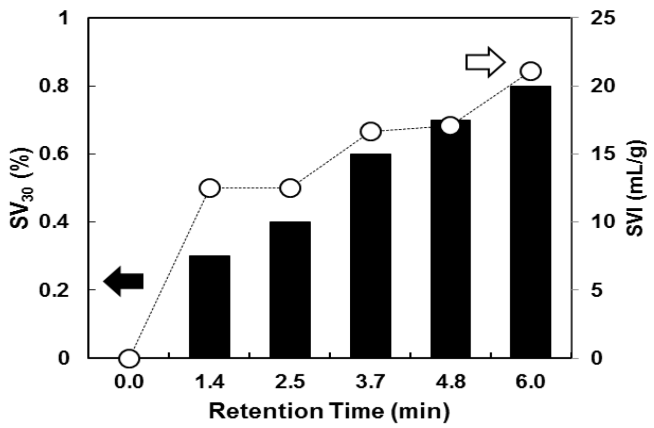


Figure 7. Variations of SV_{30} and SVI of sludge

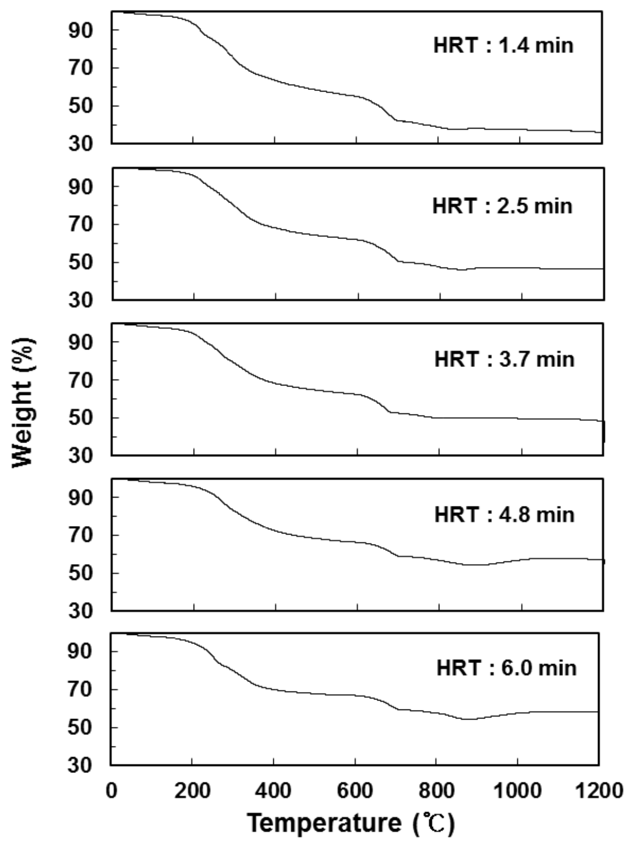


Figure 8. Thermogravimetric analysis of sludge depending on retention time

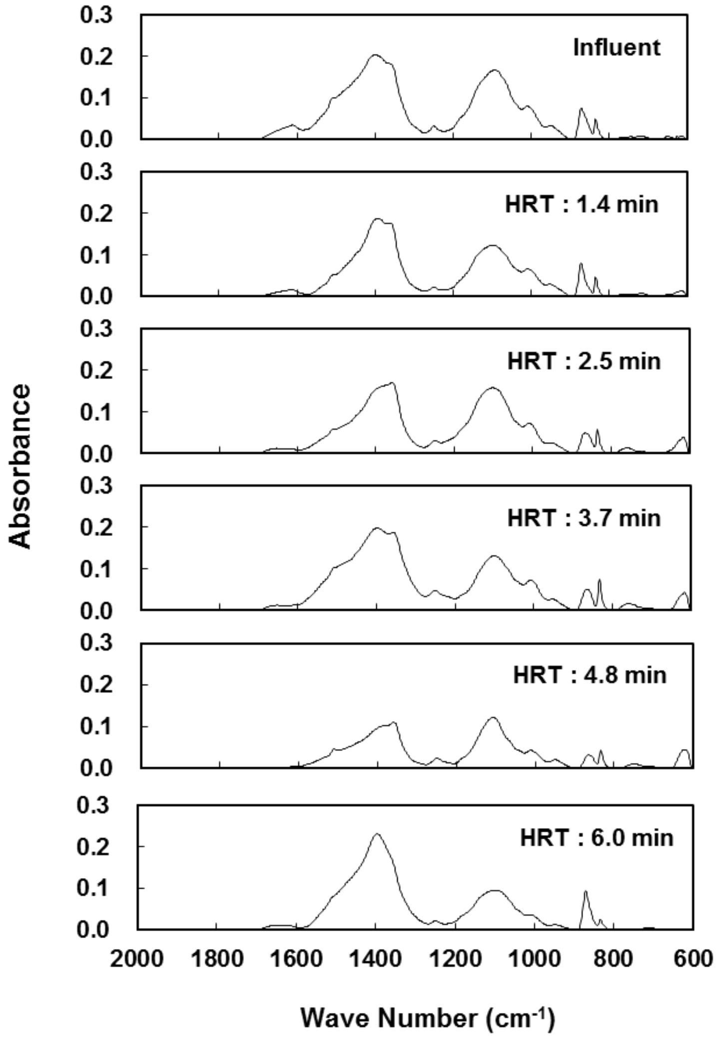


Figure 9. FT-IR Analyses of produced sludge in electrochemical treatment

Despite Removal of organics and nutrients declined after retention time of three minutes, both SV_{30} and SVI were increased linearly as retention time increased. This means that the sludge production can be affected severely rather than the pollutants concentration, and the poor settleability can be occurred by the higher sludge concentration. The SVI of 100mL/g was observed, in this study, and then the higher settling performance could be achieved successfully.

The result of thermogravimetric analysis (TGA) was illustrated in Figure 8. Weight reduction of the sludge declined as increment of retention time. The portion of organic pollutants in sludge declined because pollutants which were removed by electro-coagulation decreased in the water while sludge was produced consistently during treatment.

The laundry wastewater contains many kinds of surfactants. Figure 9 shows the sludge analyses by FT-IR depending on retention time. The peaks were spread in the wide range of wave number. The wave number ranges of 800-900, 900-1200 and 1300-1600 cm^{-1} had higher peaks than any other wave number range. Kinds of esters, amines, and aromatics would respond these wave number ranges, thus mostly they consisted of organics and nutrients in wastewater. The heights of peaks changed during treatment, it would be estimated that the composition of organics and nutrients varied during the electrochemical treatment.

3.7 The effect of aeration for additional oxidation of organics

Insufficient removal of organics and increment of pH were problems of the electrochemical treatment process in this study. To solve these problems, additional aeration was applied after the procedure. The changes of total COD and pH were illustrated in Figure 10. The COD was reduced and pH decreased within 1 hour. A large amount of bubbles were generated during aeration. As wastewater which contains surfactants is aerated, the surfactants adsorb on the bubbles [40, 41]. The organics removal would be removed by this reaction.

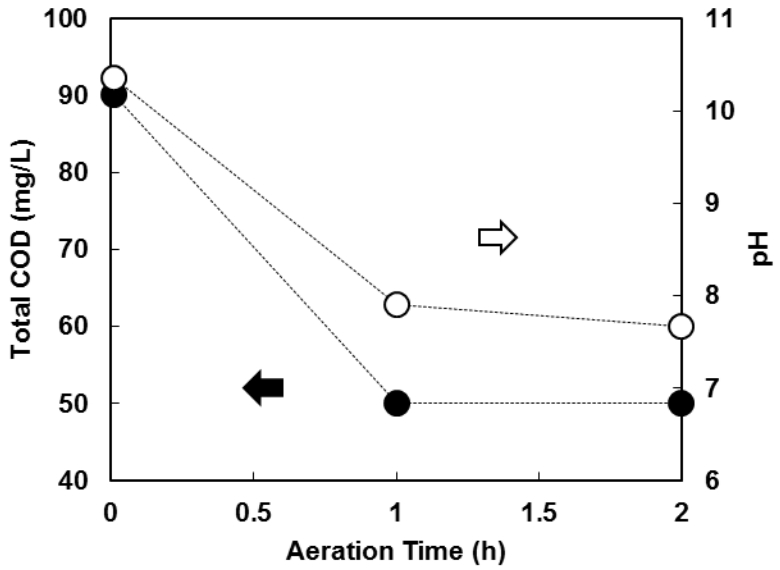


Figure 10. Variation of COD and pH by aeration for additional oxidation

Ammonium ion in the water makes chemical equilibrium with free ammonia as follow;

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \qquad (16)$$

The ammonium ion is changed to free ammonia in water of high pH. In that case, free ammonia in the water can be removed by aeration and it is called ‘ammonia stripping’. The effluent of electrochemical treatment had high pH, so ammonium would be changed the form of free ammonia and the concentration of hydroxyl ion decreases. The free ammonia is removed by aeration and residual ammonium is changed again to keep the chemical equilibrium. It would explain that pH decreased by aeration.

4. CONCLUSION

The treatability of organics and nutrients in the laundry wastewater was evaluated by using of enhanced electrochemical treatment process installed copper electrodes under the conditions of adjustable current and constant voltage. The removal of organics and nutrients could be performed in a very short time of 1.4 minutes. Even though the nitrate was removed slightly, the final effluent also guaranteed the effluent standard of wastewater treatment plant in Korea. The electrochemical treatment would be applied to advanced process of the wastewater treatment because particularly the phosphorus removal was very excellent. This process can also perform the softening by elimination of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-). The sludge, by-product of the procedure, had a good settling performance to liquid-solids separation. The final effluent can be easy to discharge by gravity settling or membrane separation.

The extension of retention time is helpful to improve the removal of pollutants, however, suitable retention time should be considered. The aeration after procedure was a sufficient solution neutralizing the pH of final effluent and removing the additional organics. This easy solution would be also polishing procedure to residual ammonia nitrogen after electrochemical treatment.

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