Agro-industrial Wastewater Treatment by Electrolysis Technology

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A modified electrolysis system was devised adopting a novel operation method of a low current and constant voltage, and a renewable copper electrode. The simultaneous removal of organics and nutrients in agro-industrial wastewater was evaluated, the analysis of by-product from electrolysis using copper electrode was also conducted. The total nitrogen decreased rapidly as the electrolysis was processed, and it was mostly performed by the elimination of ammonia nitrogen. The phosphate in water could be also removed by formation of copper compounds on the surface of the anode. Both pH value and alkalinity increased, because the concentration increment of hydroxyl ion by electrolysis of water. The ORP value also decreased during the electrolysis procedure by the generation of hydrogen gas, hydroxyl ion, and electron. The electrical conductivity as well as salinity was decreased through the electrolysis procedure, because of the loss of electrolyte ions in the wastewater through the formation of compounds and its sedimentation. The aeration was conducted for 2hours after the electrolysis procedure for the promotion of additional nitrogen removal, and the nitrogen removal could be successfully achieved. The pH value was controlled successfully to neutral with pH range of 6~8 by the aeration.

Keywords: Electrolysis, Agro-industrial wastewater, small-scale wastewater treatment, Phosphorus, Nitrogen
1. INTRODUCTION

In recent years, the importance of water environment has remarkably emerged as a major issue because of explosive population growth and industrialization. Eutrophication is a typical example of water environmental problems caused by human activities. Both nitrogen and phosphorus are essential nutrients which prompt the growth of photosynthetic algae and other photosynthetic aquatic life, leading to the acceleration of eutrophication and excessive loss of oxygen resources [1-3]. Where control of algae growth in water resources is necessary, the removal of nutrients in wastewater should be indispensable.

Nutrients removal from wastewater is generally conducted by two conventional methods. Both biological nutrient removal (BNR) and chemical precipitation by addition of metal salts such as iron and aluminum salts are the most commonly used methods for removal of phosphate from municipal and industrial wastewater [4, 5]. However, nutrients removal by chemical precipitation has some disadvantages, e.g., problems associated with the handling of chemicals, higher maintenance cost, and the disposal of large amounts of produced sludge [6]. The BNR method with internal sludge and nitrate recycling, especially in small-scale communities such as agro-industrial complexes, also has limitations of reliability and flexibility due to fluctuation of influent loading, low influent concentration, and operating complications.

The wastewater originating from agro-food industries contains proteins, sugars, oils and greases. These industries are predominantly loaded with organic wastes and are rich in organic content. The disposal of these effluents in the environment will lead to surface and groundwater contamination: increase in chemical oxygen demand, eutrophication, ecosystem imbalance and human health risks. Moreover, the ever-stringent regulatory norms make wastewater treatment a necessity [7]. Agro-food wastewater treatment has been extensively studied in conventional biological treatment systems, mainly under aerobic conditions [8, 9]. In most cases, the substrates were not readily biodegradable and therefore high biomass concentrations and hydraulic retention times were required for degradation [10]. Generally, biological processes (aerobic or anaerobic systems) are widely used for the treatment of agro-industrial wastewaters, which contain high concentrations of biodegradable organic matter (in terms of BOD) [11]. Even though biological processes are effective and economical, long hydraulic retention time and large area requirements (i.e. large volume of the bioreactor) make these processes sometimes less attractive than physico-chemical treatments, which require shorter retention time [7].

Lately, the applications of electrochemistry for environmental pollution abatement have been thoroughly investigated [12]. The electrochemical process is a very attractive method to extirpate just about any pollutant in water and wastewater involving extremely small particles or toxic organic compounds, and it can dissolve even water itself because of the electrochemical characteristics of these substances. A number of electrochemical processes have been derived to remove deleterious or dispensable constituents in water, for example, electro-oxidation [13, 14], electro-degradation [15, 16], electro-coagulation [17-19], electro-flocculation [20], electro-Fenton process [21, 22], and so on.

Electrochemical technologies such as electrolysis have been successfully employed for the treatment of many wastewaters on an industrial scale, for example, oil and grease (O&G) containing wastewaters. The electrochemical technologies have reached such a state that they are not only...
comparable with other technologies in terms of cost but also are more efficient and more compact [23, 24]. Existing electrolysis technologies are operated under constant current and adjustable voltage conditions because of the treatment of high concentration non-degradable organic wastewater. However, existing technologies have problems such as complicated electrical authentication of facilities, over-consuming of electric power with no consideration of the concentration of influent, and dangers such as electric shock injury accidents. In the electrolysis process for wastewater treatment, there are additionally important limitations such as the management and substitution of consumptive metal electrode, and operation in a fed-batch manner.

The stability of metal electrode in water depends on its corrosion characteristics, the redox potential. Most electrochemical processes use a couple of metallic electrodes, usually a relatively stable anode such as titanium and a relatively active cathode such as aluminum and iron. The redox potentials of aluminum, iron, and copper are \(-1.662V\) for \(Al=Al^{3+}+3e^-\), \(-0.440V\) for \(Fe=Fe^{2+}+2e^-\), and \(+0.337V\) for \(Cu=Cu^{2+}+2e^-\). The more positive potential is referred to as more noble, whereas the more negative potential is referred to as more active [25]. Therefore, copper is noble like gold but aluminum and iron are easily oxidized. Such active metals can be rapidly ionized at the cathode for electrolysis of wastewater. The metal ions ejected from the cathode make various compounds with the negative ions such as phosphate in wastewater and act as a coagulant. However, it is generally difficult to manage the electrodes for practical application of the electrolysis process for wastewater treatment because the cathode made of aluminum or iron is easily corroded with formation of surface scale and quick exhaustion. In this research, a modified electrolysis system was devised adopting a novel operation method using low current and constant voltage, and a renewable copper electrode. The simultaneous removal of organics and nutrients in agro-industrial wastewater was evaluated, and the analysis of by-products from electrolysis using the copper electrode was also conducted in detail.

2. EXPERIMENTAL

The continuous electrolysis system devised in this study is comprised of three parts: reactor for electrolysis, power supply, and pneumatic cleaning system, as illustrated in Figure 1. The electrolysis reactor consists of three trains having a total liquid volume of 2L, and each individual train was 250mm long and 40mm wide with a height of 1,200mm. The three 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 twenty floors. Each module was 250mm long and 40mm wide with a height of 110mm.

Each floor had three electrodes array which was composed of a cathode at the center part and two anodes at both sides of the cathode. The electrode gap between the cathode and anode was 7.5mm. A metal electrode made of copper was used, and the length of each electrode with a width of 10mm was 190mm. 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, driven by pneumatic power using nitrogen gas, undertook a scraping with a brush for all cassettes.

**Figure 1.** Schematic Diagram of continuous electrolysis system
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.

Influent wastewater was collected directly from the discharge line in the agro-industrial complex located at Yeongwo1 in Korea. There were various factories in the complex for marine products, bakery goods, clothes, machines, materials and so on. A membrane bio reactor (BMR) process for advanced wastewater treatment with a capacity of 430m$^3$/d was operated in the agro-industrial complex. The COD, total nitrogen (TN), and total phosphorus (TP) of the agro-industrial wastewater ranged between 1,250~1,810 mg/L (average 1,720 mg/L), 32.2~47.8 mg/L (average 42.2 mg/L), and 6.5~12.9 mg/L (average 11.3 mg/L), respectively. All analyses were conducted as per procedures in the American Public Health Association (APHA) Standard Methods [26]. Overall effluent was analyzed after settling for detailed observation of performance by electrolysis only. 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

In small-sized agro-industrial wastewater treatment communities operated with biological treatment processes, the control and guarantee of effluent quality is very difficult because of the fluctuation of influent quality and flowrate. Therefore, the physico-chemical process such as electrolysis can be a useful candidate for the treatment of agro-industrial wastewater [7]. The influent wastewater and electrolyzed effluents, as shown in Figure 2(a), and the distilled water are displayed together to compare the color among influent and effluents. The color of influent wastewater was brown and the primarily electrolyzed effluent showed a green color. The color of secondary effluent treated in the second train also became bluish green and that of the tertiary effluent was blue.

The electrolysis results in the decomposition of water into H$_2$ at the cathode and O$_2$ at the anode by an electric current being passed through the water. A reduction reaction occurs at the cathode such as $2H^+(aq) + 2e^- \rightarrow H_2(g)$, and an oxidation reaction takes place at the anode such as $2H_2O(l) \rightarrow O_2(g) + 4 H^+(aq) + 4e^-$. In case of wastewater, the various pollutants become electrolytes and lower the electrical resistance in water. The electrolytes disassociate into cations, which move to the cathode, and anions, which travel to the anode, thus allowing continuous electrical flow in the water. An anion from the electrolyte will lose an electron and be oxidized when the electrolyte anion has less standard
electrode potential than the hydroxide. A cation with a greater standard electrode potential than the hydrogen ion will also be reduced.

Figure 2. Photographs of influent and effluents (a) Influent wastewater and electrolyzed effluents before settling (b) Electrolyzed effluents after settling
In this study, where the copper electrode was used for the treatment of agro-industrial wastewater including phosphate compounds, by-products such as copper phosphate ($\text{Cu}_3(\text{PO}_4)_2$) and phosphorus oxide ($\text{P}_2\text{O}_5$) with pale blue color formed on the surface of the anode and bubbles of hydrogen gas formed on the surface of the cathode. Although the effluent gradually changed color from brown to blue through the electrolysis procedure, it should be noted that the phosphate ions ($\text{PO}_4^{3-}$) in the water could be removed by formation of copper compounds on the surface of the anode. Figure 2(b) presents the settled effluents, of which the sediments could be separated well during the shorter settling time of 30min. The supernatants became clear and transparent with longer settling time and sediments of by-products gradually piled up. The color change of the sediments was similar to that of effluents before settling, as mentioned in Figure 2(a), because of precipitation of copper phosphate ($\text{Cu}_3(\text{PO}_4)_2$) and phosphorus oxide ($\text{P}_2\text{O}_5$) removed from the surface of the anode.

![Figure 3. Changes of conductivity and salinity during the electrolysis procedure](image)

In general, the correlation between the electrical conductivity and salinity is proportional to the concentration of electrolyte ions [27]. Figure 3 shows the electrical conductivity and salinity in both influent wastewater and electrolyzed effluents, and the conductivity as well as salinity gradually decreased through the electrolysis procedure. The decrease of conductivity can be explained by the loss of electrolyte ions in the wastewater through the formation of various compounds and its sedimentation. Also, it could be considered that the chloride ion was transformed into chlorine gas ($\text{Cl}_2$) after playing the role of electron donor. According to Costaz [28], and Krstajic and Nakic [29], the chloride ion in the saline wastewater was converted anodically to chlorine which is further converted to hypochlorous acid in the aqueous solution. The change in current value gave evidence for the explanation of the above results. As the electrolysis procedure progressed, the dramatic reduction of current value in the system could be observed from around 4.5A to 3.5A under the condition of constant bias voltage of 24V by the removal of electrolytes in wastewater.
The variation of nitrogen concentration during the electrolysis procedure is presented in Figure 4. The total nitrogen decreased rapidly as electrolysis processed, and this occurred by the elimination of ammonia nitrogen, as shown in Figure 4. Generally, the removal of ammonia nitrogen by electro-oxidation includes the direct and indirect oxidation reactions [30]. 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. The chloride ions (Cl\(^-\)) included in the wastewater can lose electrons at the anode and then be removed as chlorine gas (Cl\(_2\)). Hypochlorous acid (HOCl) is formed from the dissolved chlorine ions in wastewater after the deaeration to chlorine gas as follows:

\[
2\text{Cl}^-\rightarrow\text{Cl}_2+2e^- \quad \text{(1)}
\]

\[
\text{Cl}_2+\text{H}_2\text{O}\rightarrow\text{HOCl}+\text{H}^++\text{Cl}^- \quad \text{(2)}
\]

The hypochlorous acid reacts with the ammonium ion as follows, and finally the ammonium ion is stripped into nitrogen gas.

\[
2\text{NH}_4^++3\text{HOCl}\rightarrow\text{N}_2+3\text{H}_2\text{O}+5\text{H}^++3\text{Cl}^- \quad \text{(3)}
\]

![Figure 4. Effect of the electrolysis on nitrogen removal](image)

Also, the removal rate of ammonia nitrogen decreased as electrolysis processed. It may be explained that the dissolved ammonium ions existed in the form of free ammonia with increased pH during the electrolysis process, and then the concentration of ammonia nitrogen which can react with the hypochlorous acid steadily decreased. The concentration of nitrate (NO\(_3^-\)) slightly increased, because the nitrate was formed by the reaction between the hypochlorous acid and the ammonium ion as follows;
0.25NH_4^+ + HOCl → 0.25NO_3^- + 0.25H_2O + 1.5H^+ + Cl^- (4)

Figure 5 shows the changes of phosphorus concentration in the electrolysis experiments using the copper electrode. The phosphorus was mostly removed from 11.3mg/L to 0.15mg/L during the shorter reaction time of around 1.5 minutes through the formation of copper phosphate (Cu_3(PO_4)_2) and phosphorus oxide (P_2O_5) at the anode.

\[ \text{Figure 5. Effect of the electrolysis on phosphorus removal} \]

The phosphorus concentration in typical agro-industrial wastewater in Korea is below 10mg/L, so that this continuous electrolysis system with the copper electrode can be an excellent candidate to replace existing phosphorus removal techniques. Phosphorus removal by electrolysis using the copper electrode can be performed in combination with the copper ion and orthophosphate as follows, and by adsorption with copper hydroxide as the case maybe.

\[ \text{Cu(s)} + 2\text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 4\text{H}^+ + \text{O}_2 + 2\text{e}^- \] (5)

\[ \text{Cu}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Cu}_3(\text{PO}_4)_2\text{(s)} \downarrow \] (6)

\[ \text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2\text{(s)} \downarrow \] (7)

Figure 6 presents the variation of pH value and alkalinity in both influent wastewater and electrolyzed effluents, with both having remarkably increased as electrolysis processed. It seems that the concentration increment of the hydroxyl ion (OH^-) in water would induce the proportional enhancement of alkalinity through the hydroxyl ion generated at the anode by electrolysis. Various studies have also shown similar with our results on the change of pH values after electrolysis [31, 32]. The pH value recorded after electrolysis or electrocoagulation increased rapidly.
The result of pH increment by hydroxyl ion (OH\(^-\)) generated at the cathode can be also explained in relation to the ORP change by electrolysis. The oxidation reduction potential (ORP) represents whether the main reaction in water is oxidation or reduction. Figure 7 presents the variation of ORP, and the ORP value gradually decreased during the electrolysis procedure. It could be considered that the increment of pH value and drop of ORP value caused by the generation of hydrogen gas (H\(_2\)), hydroxyl ion (OH\(^-\)), and electron (e\(^-\)), because the electrolysis results in the decomposition of water into hydroxyl ion (OH\(^-\)) and hydrogen gas (H\(_2\)) at the cathode and electron (e\(^-\))
at the anode. This is in agreement with the results of Israilides et. al [32] according to whom during the electrolysis of alkaline solutions hydroxyl radicals are formed which are capable of oxidizing to a great extent the organic matter, and for this reason they have a very short life so reducing the total oxidation potential of the solution.

The total nitrogen rapidly decreased by elimination of ammonia nitrogen during electrolysis, as discussed in Figure 4. However, the total nitrogen concentration of around 24mg/L remained. Hence, aeration was conducted for 2 hours after the electrolysis procedure for control of the pH value and promotion of additional nitrogen removal. Figure 8 shows the change of nitrogen concentration by post-aeration, and it is apparent that additional nitrogen removal may be successfully achieved. The removal of ammonia nitrogen, which was the major component of total nitrogen removal, could be performed during progress of aeration as revealed. In general, nitrogen exists in water in two forms; both free ammonia and ammonium ion, and they are in equilibrium in water as follows:

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (8)
\]

When the aeration is conducted under condition of high pH, the free ammonium can be stripped; the ammonia stripping for nitrogen removal is commonly accomplished at pH 11 [33]. In this experiment, the higher pH value elevated by the electrolysis process may be sufficiently decreased by the stripping of free ammonia.

![Figure 8](image-url)

**Figure 8.** Change of nitrogen concentration by the post-aeration

Figure 9 shows the results of Fourier transform infrared spectroscopy (FT-IR), for which the samples were prepared on quartz glasses with dried water drops. The influent included saturated hydrocarbon compounds including nitrogen. The compounds were mixed in a very complicated
manner, so that the peak was very broad, which made peak indexing not easy. Through electrolysis of wastewater, the compounds were changed as depicted in Figure 9. The peak for saturated hydrocarbon compounds in the influent was divided and sharp, which means the compounds would be dissolved into more simple structures and oxygen would also be included. Consequently, the compounds should be oxidized during the electrolysis process. Such oxidation results for the organics in the influent through electrolysis, corresponds to the previous discussion in this paper.

![Figure 9. FT-IR of electrolyzed effluent](image)

**Table 1.** ICP result of influent wastewater and electrolyzed effluent

<table>
<thead>
<tr>
<th></th>
<th>Influent wastewater (ppm)</th>
<th>Primary effluent (ppm)</th>
<th>Secondary effluent (ppm)</th>
<th>Tertiary effluent (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
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<td>0.075</td>
<td>0.160</td>
<td>0.180</td>
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<tr>
<td>As</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>B</td>
<td>0.336</td>
<td>0.133</td>
<td>0.101</td>
<td>0.089</td>
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<tr>
<td>Ca</td>
<td>19.642</td>
<td>42.324</td>
<td>20.491</td>
<td>6.434</td>
</tr>
<tr>
<td>Cd</td>
<td>0.001</td>
<td>0.005</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Cu</td>
<td>5.632</td>
<td>5.351</td>
<td>4.312</td>
<td>2.639</td>
</tr>
<tr>
<td>Fe</td>
<td>0.069</td>
<td>0.010</td>
<td>0.010</td>
<td>0.048</td>
</tr>
<tr>
<td>K</td>
<td>12.677</td>
<td>40.310</td>
<td>38.928</td>
<td>36.034</td>
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<tr>
<td>Mg</td>
<td>6.612</td>
<td>17.533</td>
<td>8.545</td>
<td>3.561</td>
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<td>422.575</td>
<td>414.730</td>
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<tr>
<td>P</td>
<td>3.113</td>
<td>0.194</td>
<td>0.124</td>
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<tr>
<td>Pb</td>
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<td>0.003</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>S</td>
<td>1.265</td>
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<td>2.340</td>
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<tr>
<td>Si</td>
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<td>Zn</td>
<td>0.069</td>
<td>0.030</td>
<td>0.017</td>
<td>0.022</td>
</tr>
</tbody>
</table>
Table 1 is the result of inductively coupled plasma emission spectroscopy (ICP-ES) of the influent wastewater and electrolyzed effluents to research metal ions. The samples were prepared by filtration of 0.4μm filter papers. The metals resulting from ICP-ES analysis would be ions or included in small particles less than 0.4μm in diameter. The amount of metals was not so different over all. In particular, the phosphorus content was reduced by electrolysis from 3.1 to 0.1 ppm, as discussed above. The copper could be easily detected after electrolysis because it was used as an electrode. However, the copper content decreased, to the contrary, which was on account of the formation of copper oxide, hydroxide, or phosphate particles.

Figure 10 presents the micrographs of the by-products (sludge) from the tertiary effluent. As shown in Figure 10(a), the particles looked like inorganic powders, several micrometers in size. The sludge particles were hard aggregates of very small particles, all under one micrometer, as presented in Figure 10(b). The electrolysis eliminates the various pollutants in the wastewater by oxidation. Meanwhile, the copper compound particles are formed including pollutants like phosphorus. When the copper compound particles are agglomerated with each other, the organics may also be included into the aggregates.

![Figure 10. SEM of sludge from tertiary effluent](image)

Figure 11 presents the result of thermogravimetric analysis (TGA) of the dried sludge. When increasing the temperature to around 400°C and then slowly decreasing, the weight of the sludge was rapidly reduced. In case of the primary sludge, the weight loss was around 70%, which would be mostly organic components. The weight loss of the secondary and tertiary sludge was about 60 and 50%, respectively. This means that the removal rate of organics would be high at the initial state. Table 2 shows the ICP-ES result of the sludge. The main constituent was copper and there also was calcium, magnesium, sodium and phosphorus and so on. As discussed above, copper formed oxides, hydroxides and phosphates. Also, phosphorus could form phosphorus oxide. Consequently, the sludge consisted of copper compounds including phosphorus and organics making up over 50% in total sludge weight.
Figure 11. TGA of sludge

Table 2. ICP result of sludge

<table>
<thead>
<tr>
<th></th>
<th>Sludge from primary effluent (wt.%)</th>
<th>Sludge from secondary effluent (wt.%)</th>
<th>Sludge from tertiary effluent (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
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<td>0.593</td>
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<td>0.001</td>
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<td>Cu</td>
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<td>Fe</td>
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<tr>
<td>Zn</td>
<td>0.131</td>
<td>0.111</td>
<td>0.107</td>
</tr>
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</table>
4. CONCLUSION

In this study, a modified electrolysis system was devised adopting a novel operation method of a low current and constant voltage, and a renewable copper electrode. The simultaneous removal of organics and nutrients in agro-industrial wastewater was evaluated, the analysis of by-product from electrolysis using copper electrode was also conducted. The electrical conductivity as well as salinity was gradually decreased through the electrolysis procedure, because of the loss of electrolyte ions in the wastewater through the formation of compounds and its sedimentation.

The total nitrogen decreased rapidly as the electrolysis was processed, and it was mostly performed by the elimination of ammonia nitrogen. The phosphate ions (PO\textsubscript{4}\textsuperscript{3-}) in water could be also removed by formation of copper compounds on the surface of the anode. Both pH value and alkalinity remarkably increased as electrolysis processed, because the concentration increment of hydroxyl ion by electrolysis of water. The ORP value also decreased during the electrolysis procedure by the generation of hydrogen gas, hydroxyl ion, and electron. The aeration was conducted for 2 hours after the electrolysis procedure for the promotion of additional nitrogen removal, and the nitrogen removal could be successfully achieved. The pH value was controlled successfully to neutral with pH range of 6~8 by the aeration.

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