Int. J. Electrochem. Sci., 8 **(2013)** 8557 - 8571

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrolytic Removal of Phosphorus in Wastewater with Noble Electrode under the Conditions of Low Current and Constant Voltage

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Received: 2 April 2013 / *Accepted:* 14 May 2013 / *Published:* 1 June 2013

Electrochemical experiment using three cathode materials such aluminum, iron, and copper operated constant voltage and low current conditions to evaluate the removal characteristics of phosphate ion in wastewater. The electrolysis experiments on synthetic wastewater with a higher concentration were also repeated 200 times for 10 minutes per each experiment under the bias voltage of 24V to estimate the stability of the copper electrode for a long time. When the copper electrode couple was used, by-products with green blue color such as copper hydroxide ($Cu(OH)_2$) and copper phosphate ($Cu_3(PO_4)_2$) were formed on the surface of the anode and bubbles of hydrogen gas were formed on the surface of the cathode. The formation of copper hydroxide could contribute to removing phosphate because the hydroxyl ion (OH^-) in the copper hydroxide can be exchanged with the phosphate ion. The surface of the copper anode was relatively clean without oxidation, while the surfaces of the aluminum and iron anodes were completely changed from the initial state with severe oxidation. With such change to the anode surface such as aluminum and iron anodes, the electrolysis performance would degrade very fast. In repeated electrolysis experiment using the copper electrode on synthetic wastewater with a higher concentration, the copper anode of 1mm thickness was sufficient to remove the phosphate which was more than 19g.

Keywords: Electrolysis, Electrode, Constant voltage, Phosphorus removal, Wastewater treatment

1. INTRODUCTION

Nutrients such as nitrogen and phosphorus are essential to the growth of algae and other biological organisms. The nutrients are necessary to stimulate the growth of photosynthetic algae and other photosynthetic aquatic life which leads to accelerated eutrophication and excessive loss of oxygen resources [1–3]. Eutrophication can be prohibited 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. Therefore, there is presently much interest in controlling the amount of phosphorus compounds that enter surface waters in domestic and industrial waste discharges and natural runoff.

The usual forms of phosphorus that are found in aqueous solutions include orthophosphate, polyphosphate, and organic phosphate. In general, phosphorus removal is performed by two conventional methods from wastewater. Both chemical precipitation by addition of metal salts such as iron and aluminum salts, and biological treatment are the most commonly used methods for removal of phosphate from municipal and industrial wastewater [4, 5]. However, chemical precipitation has some disadvantages, e.g., higher maintenance cost, problems associated with the handling of chemicals, and the disposal of large amounts of produced sludge. Biological treatment also requires a highly efficient secondary clarifier and sufficient organic concentration for consumption by microorganisms [6, 7].

In recent years, there have been many efforts to find a new approach for phosphorus removal [8]. The electrochemical process is a very useful method to extirpate just about any pollutant in water and wastewater involving extremely small particles, toxic organic compounds, and it can dissolve even water itself because of the electrochemical characteristics of substances. A number of electrochemical processes have been derived to remove deleterious or dispensable constituents in water and wastewater, for example, electro-oxidation [9-12], electro-degradation [13-15], electro-coagulation [16-23], electro-flocculation [24], the electro-Fenton process [25-29], and so on. Most electrochemical processes use a couple of metallic electrodes, usually a relatively stable cathode such as titanium and a relatively active anode 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 $Cu=Cu^{2+}+2e^{-}$, respectively. The more positive potential is referred to as more noble, whereas the more negative potential is referred to as more active [30]. 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.

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 limitations 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 this study, a low current and constant voltage method was applied to electrolysis to overcome the disadvantages of existing electrolysis technologies, and the electrochemical experiment using three cathode materials such as aluminum, iron, and copper was performed to evaluate the removal characteristics of phosphate ion in wastewater.

2. EXPERIMENTAL

An electrolysis cell was simply composed of a mass cylinder of 100mL and a couple of electrodes with a power supply as illustrated in Figure 1. The metal electrodes made of copper, aluminum, and irons were used for the performance evaluation of each electrode, respectively. The length of each electrode with a width of 7.5mm was 170mm, and most of the electrode was immersed in synthetic wastewater. The electrode gap between the anode and cathode was 7.5mm, and the pair of electrodes was fixed by a plastic clip.

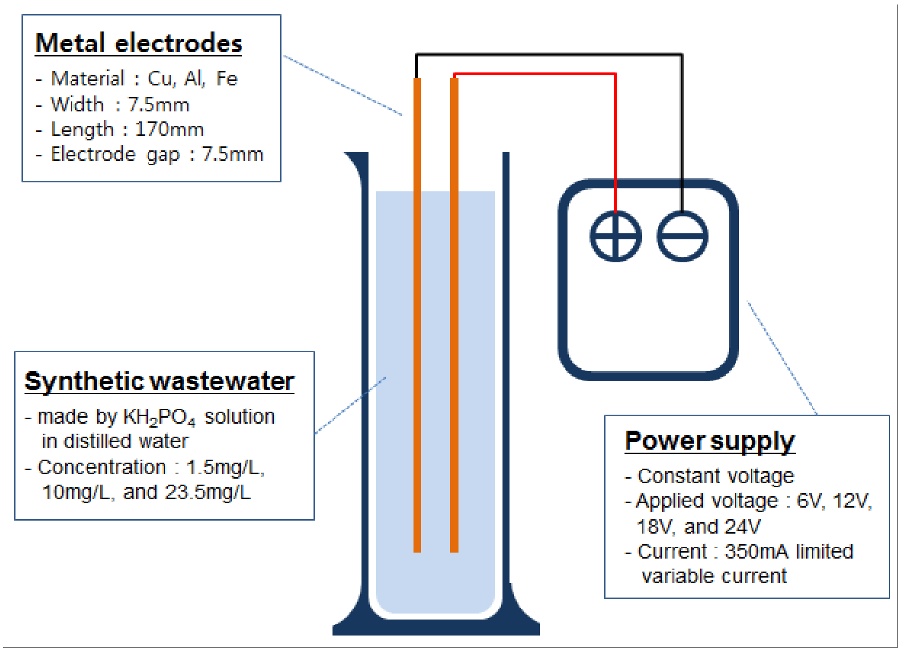


Figure 1. Schematic diagram of electrolysis experiment

The synthetic wastewaters with phosphorus concentrations of 1.5mg/L, 10mg/L, and 25mg/L were prepared by solution of KH_2PO_4 in distilled water. 100mL of synthetic wastewater was used for each electrolysis experiment. Measurement of phosphate was conducted using the ascorbic acid method from the American Public Health Association (APHA) Standard Methods [31].

The electrolysis experiment was performed under constant voltage and variable current with an upper limit of 350mA. The bias voltage range was from 6V to 24V and the applied time range was up to 30 minutes. During the electrolysis procedure, the current value between the anode and cathode was simultaneously measured. After the electrolysis, the pH and phosphate concentration of each effluent was also measured. To estimate the stability of the copper electrode for a long time, the electrolysis experiments on synthetic wastewater with a higher concentration of 100mg/L were repeated 200 times for 10 minutes per each experiment under the bias voltage of 24V. After the electrolysis experiment, the by-product, i.e. the sludge, was dried and analyzed by X-ray diffraction (XRD, 400K, JEOL, JEM-4010) and transmission electron microscopy (TEM, Rigaku, D/max-2500/PC).

3. RESULTS AND DISCUSSION

Basically, electrolysis of water results in the decomposition of water into O_2 at the anode and H_2 at the cathode by an electric current being passed through the water [32]. At the cathode, a reduction reaction takes place: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ and an oxidation reaction occurs at the anode: $2 H_2O(l) \rightarrow O_2(g) + 4 H^+(aq) + 4e^-$, as shown in Figure 2. Two electrodes, typically made from some inert metal, are placed in the water and connected to an electrical power source.

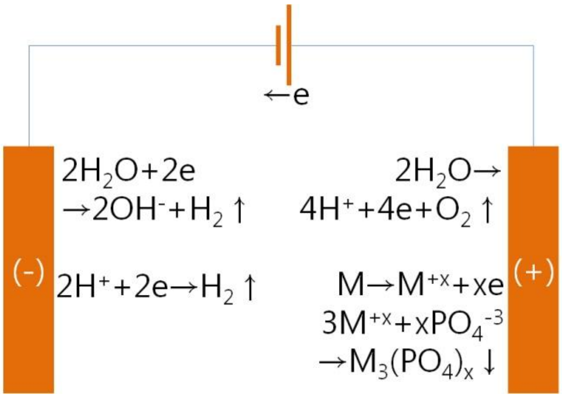


Figure 2. Schematic diagram of electrolytic reaction

Electrolysis of pure water requires excess energy to overcome various activation barriers, so the electrolysis of pure water does not occur without this excess energy. Electro catalysts are also required for electrolysis of pure water, because the electrical conductivity of pure water is very low. The efficiency of electrolysis can be enhanced by the addition of an electrolyte such as a salt, an acid or a base [33]. If there are electrolytes in the water, the conductivity of the water increases considerably. In case of wastewater, the various pollutants become electrolytes and lower the electrical resistance in the 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 [34]. In the solution of KH_2PO_4, the potassium and the hydrogen cations should go to the cathode and the hydrogen ions can get electrons. Also, the phosphate ions should go to the anode and can make insoluble compounds with metal ions having lost electrons at the anode as illustrated in Figure 2.

Figure 3 shows the electrode compositions in the electrolysis experiment (a) and the photographs of the anode surface after the electrolysis (b). In case of the copper electrode couple, green blue by-products were formed on the surface of the anode and bubbles of hydrogen gas were formed on the surface of the cathode. In the same way, white by-products on the aluminum anode and the yellow by-products on the iron anode were also produced. Normally, the color of copper oxide is black (CuO) or red (Cu_2O). Copper hydroxide ($Cu(OH)_2$) and copper phosphate ($Cu_3(PO_4)_2$) have the green blue color [35] as shown in Figure 3(a). Apparently, the by-products could be copper hydroxide or copper phosphate. The formation of copper hydroxide can contribute to removing phosphate because the hydroxyl ion (OH^-) in the copper hydroxide can be exchanged with the phosphate ion [36]. On the other hand, the white by-product on the aluminum anode was difficult to estimate because the color of aluminum oxide, the hydroxide and phosphate were all white. The yellow by-product on the iron anode was also uncertain because the iron oxide color is variable from yellow to black [35]. The surface of the copper anode was relatively clean without oxidation, while the surfaces of the aluminum and iron anodes were completely changed from the initial state with severe oxidation as shown in Figure 3(b). With such change to the anode surface, the electrolysis performance would degrade very fast. Also, the corrosion of the surface would be inhomogeneous and cause stress corrosion cracking. Consequently, the lifetime of the anode cannot be guaranteed for a long period.

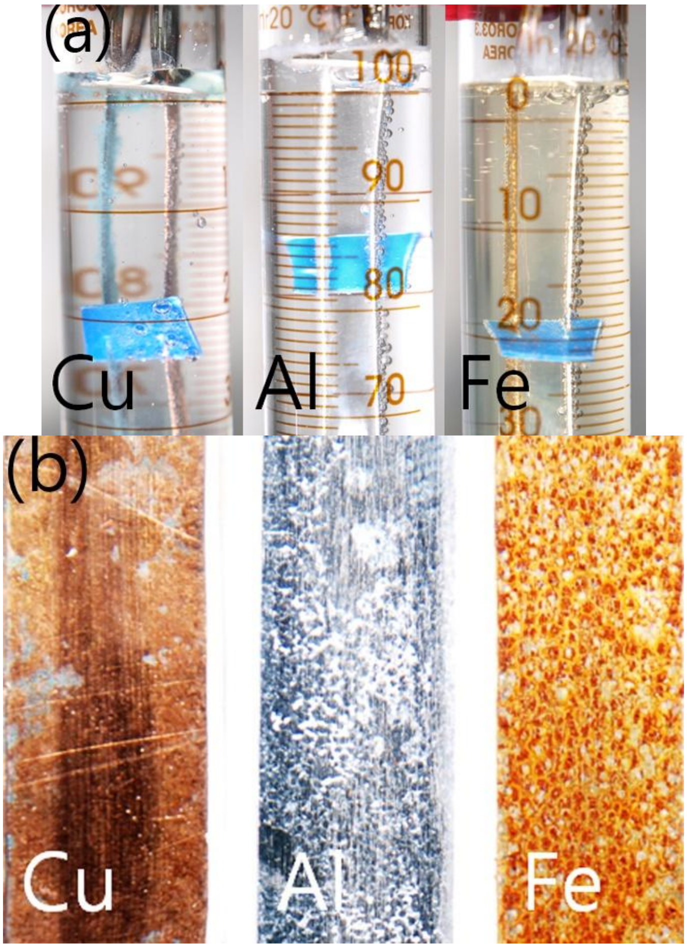


Figure 3. Photographs of (a) electrode’s setting and (b) electrode’s surfaces after experiment

Figure 4 presents the changes of phosphate concentration and current value in the electrolysis experiments using the copper electrode couple.

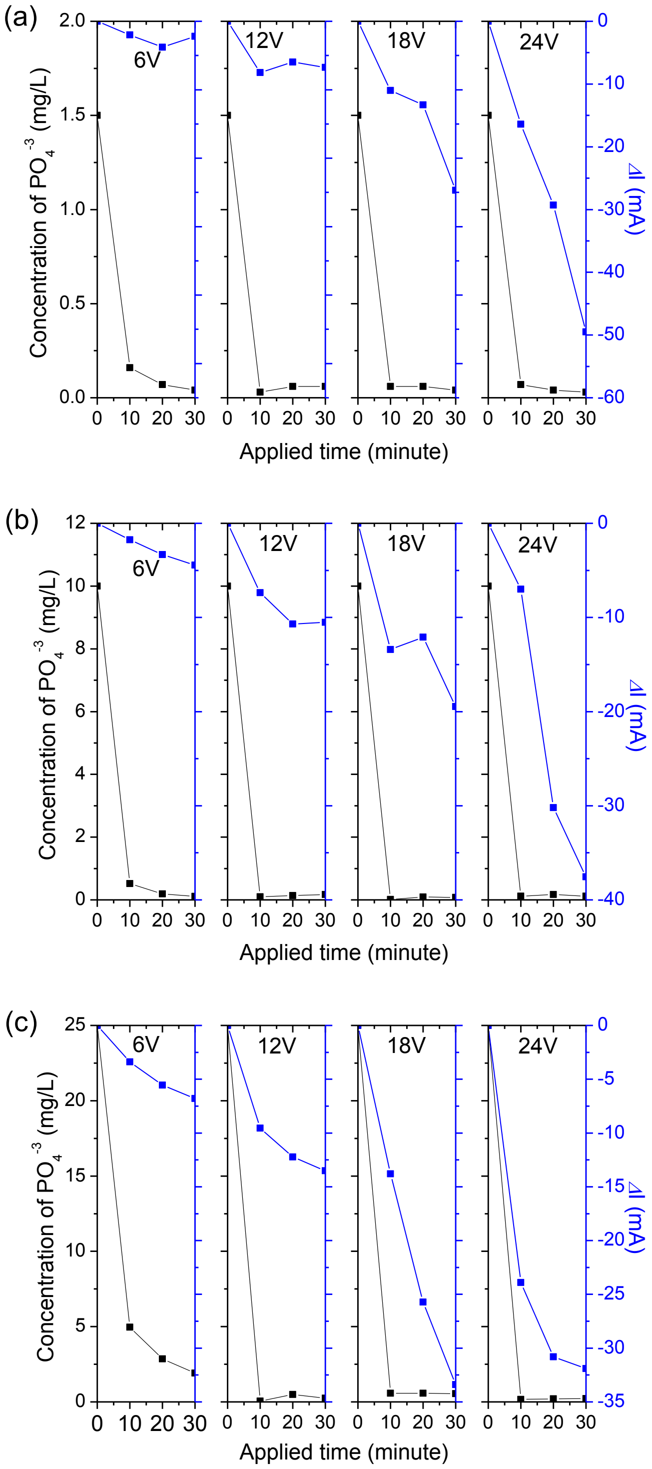
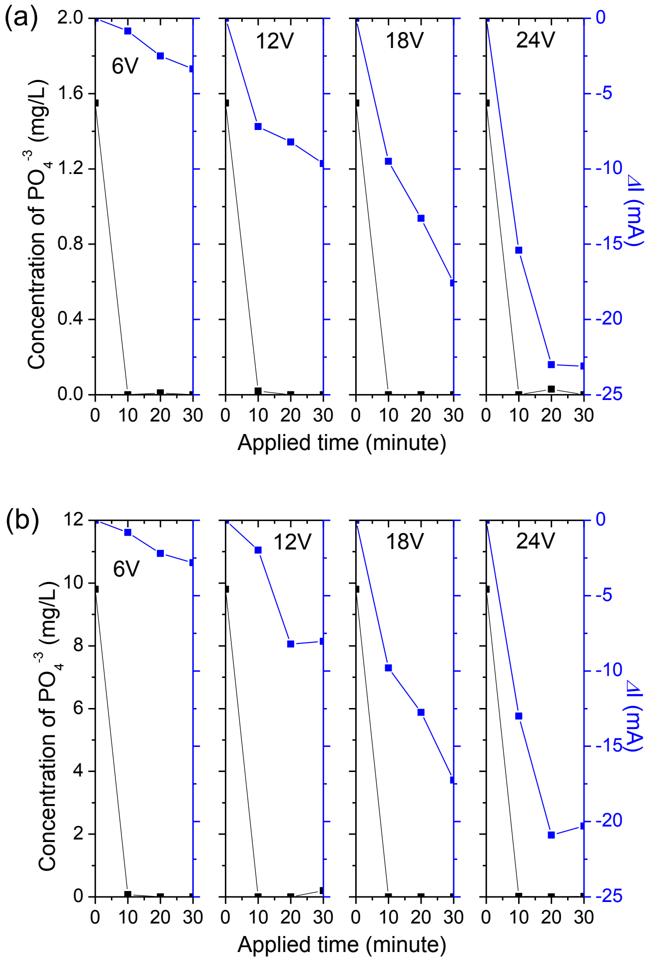


Figure 4. Changes of phosphate and current in electrolysis with copper electrode

The phosphate concentration was dramatically decreased for 10 minutes regardless of influent concentration and current value. Under the bias voltage of 6V, the phosphate concentration gradually decreased up to 30 minutes, and the removal was additionally performed at over 12V of bias voltage. Also, the current value was generally decreased during the electrolysis procedure; this means that the electrical resistance increased because the electrolytes were removed in the water. If the bias voltage is increased, the decrement of current could be increased. When bias was applied, copper atoms on the anode surface could have combined, losing electrons, with phosphate negative ions being drawn in the electric field. Consequently, the copper phosphate ($Cu_3(PO_4)_2$) or copper phosphorus oxide could have formed on the anode surface. Higher bias voltage and more active reaction of copper and phosphate could take place with the stronger electric force.

As can be seen from the results of electrolysis experiments using the aluminum electrode couple, as presented in Figure 5, the changes in phosphate concentration and current value were observed to be very similar to that of the copper one. Phosphate removal by electrolysis using the aluminum electrode couple seems to be more effective than that of copper. As mentioned above, aluminum can be easily ionized when compared to copper, so that the ionized aluminum can combine with the phosphate ion to form aluminum phosphate ($AlPO_4$). Also, aluminum can be very easily oxidized on the surface and in the water to form aluminum oxide (Al_2O_3). For phosphate removal in wastewater using a chemical, the aluminum sulfate ($Al_2(SO_4)_3$) is generally used to form a precipitate like aluminum phosphate [37].



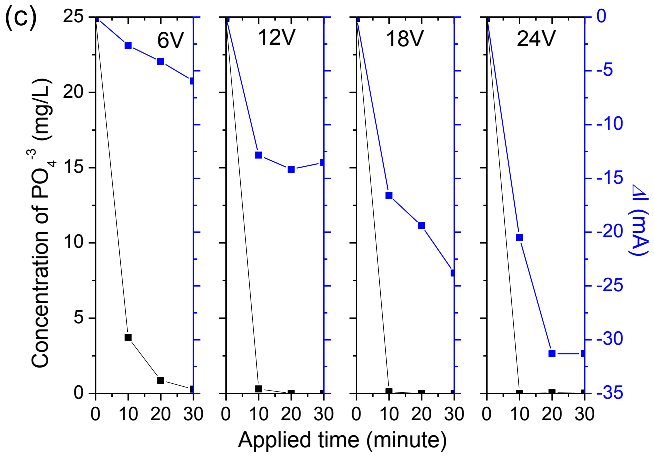
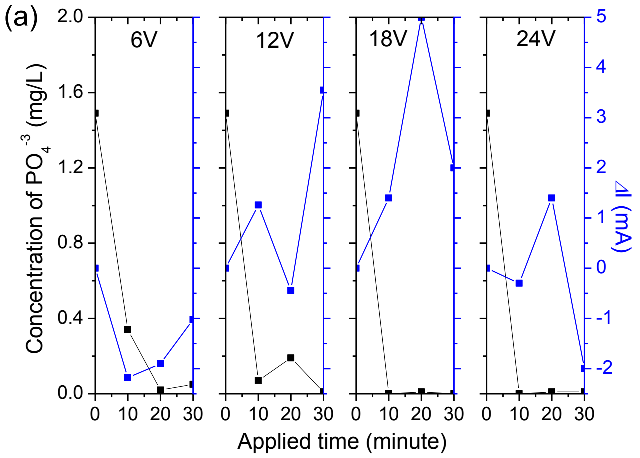


Figure 5. Changes of phosphate and current in electrolysis with aluminum electrode

Figure 6 shows the results of the electrolysis experiment using the iron electrode couple. When wastewaters with concentrations of 1.5mg/L and 10mg/L were applied, the changes in phosphate concentration were similar with each other, as presented in Figures 6(a) and (b), respectively. For wastewater with a relatively higher concentration of 25mg/L, however, sufficient phosphate removal could not be achieved regardless of the condition of higher voltages as shown in Figure 6(c). The current variation fluctuated considerably because of the severe oxidation at the iron anode surface and unnecessary excess ionization at the anode. When the aluminum electrode was applied to the experiment, excess ionization could take place more actively, while the aluminum ions immediately combined with the hydroxyl ion (OH^-) to form aluminum hydroxide ($Al(OH)_3$) [38]. Therefore, the aluminum ions could not affect the current variation such as with the iron ions. Figure 7 shows the effects of the electrolysis process on pH changes.



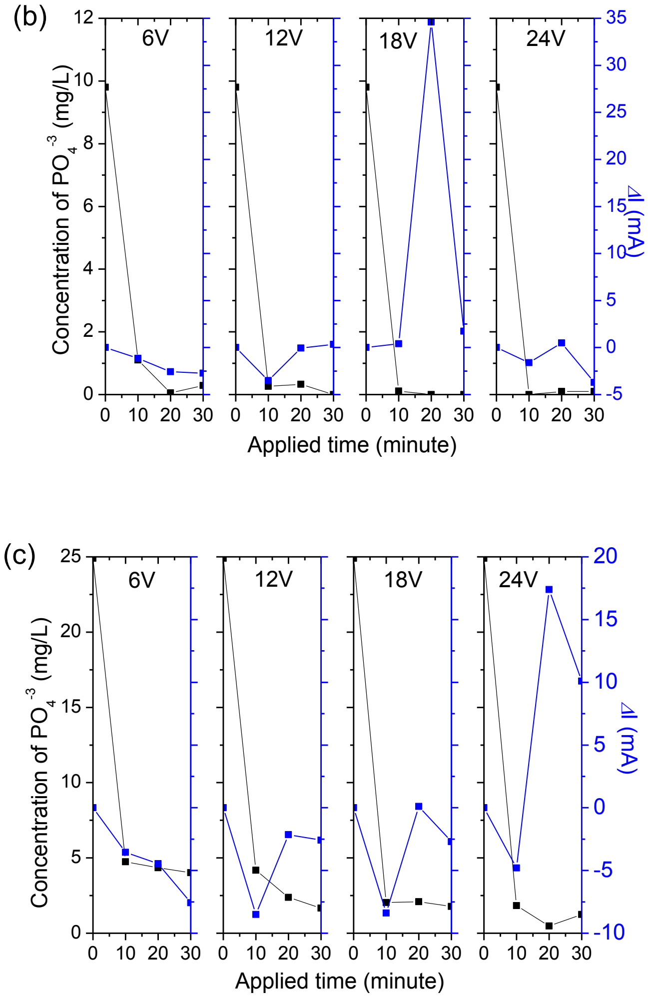


Figure 6. Changes of phosphate and current in electrolysis with iron electrode

During the initial electrolysis procedure using the copper electrode for 10 minutes, the pH value increased considerably up to over 9, which was similar in aspect to the decrement of phosphate concentration as presented in Figure 7(a). When phosphate removal in the solution was performed, the pH value became steady. In case of electrolysis using the aluminum electrode, an increase of pH to around 8~9, lower than that of the copper electrode, was observed, as shown in Figure 7(b). As mentioned above, the low concentration of hydroxyl ions may be explained by the formation of aluminum hydroxide by the excess aluminum ions. Electrolysis using the iron electrode increased the pH value up to over 9, and its change was not stable, as revealed in Figure 7(c).

Figure 8 shows the result of the repeated electrolysis experiment using the copper electrode on synthetic wastewater with a higher concentration of 100mg/L. The copper anode of 1mm thickness was sufficient to remove the phosphate which was more than 19g. Also, the electrolysis with the copper electrode to remove phosphate was stable for a long time.

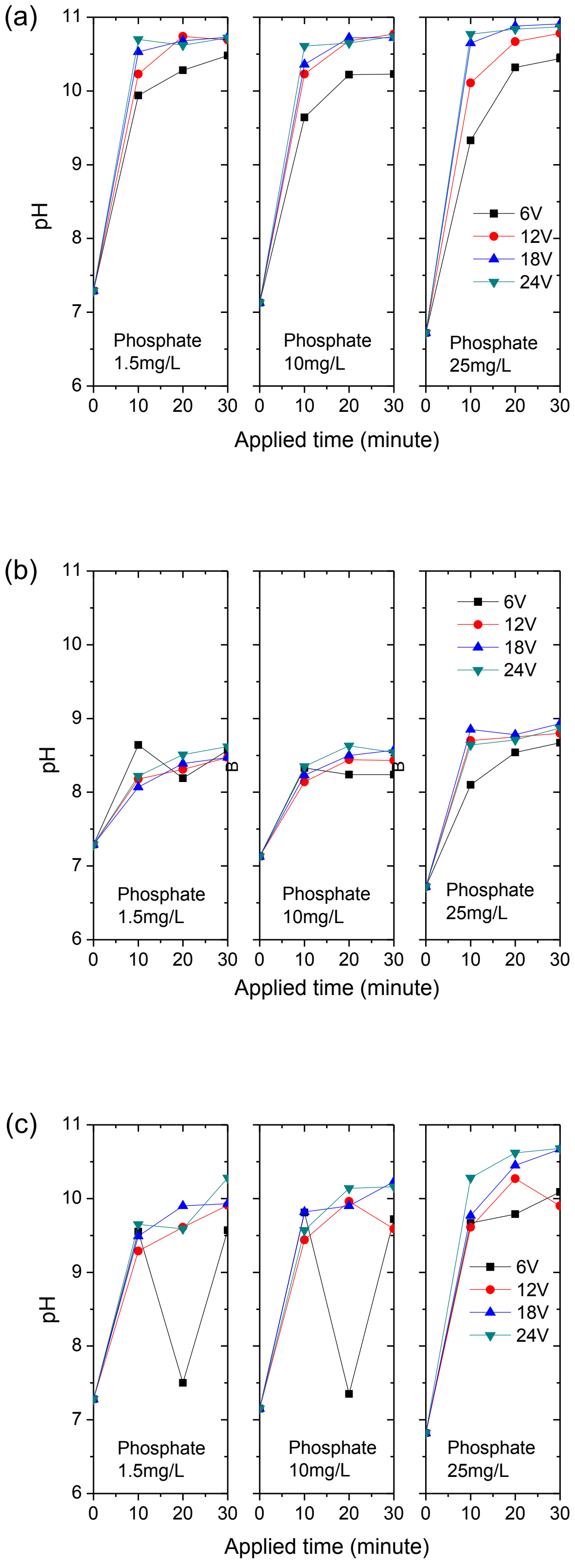


Figure 7. Changes of pH value in electrolytic process with (a) copper, (b) aluminum, and (c) iron electrodes

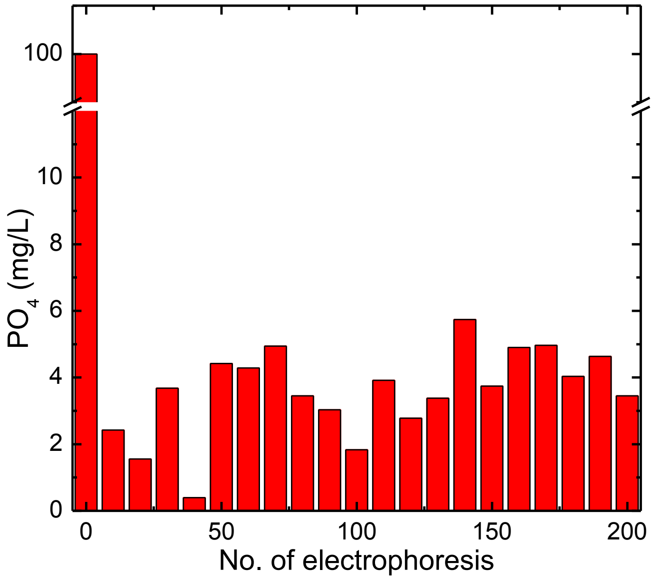


Figure 8. Durability of copper electrode for phosphate removal process

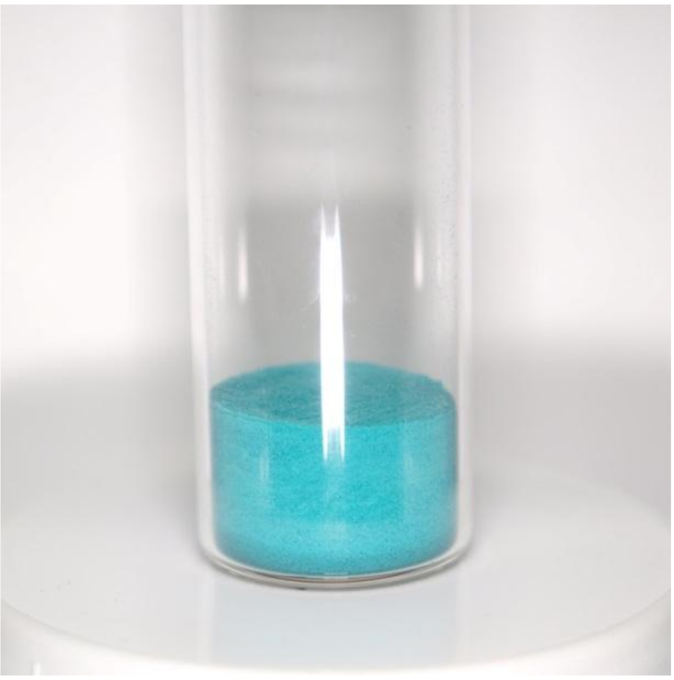


Figure 9. Photograph of sediment by electrolytic process with copper electrode in phosphate water solution

Figure 9 is the photograph of the by-product from the electrolysis experiment using the copper electrode. Apparently, it consists of copper compounds including copper phosphate, copper phosphorus oxide, or copper hydroxide. The by-products were thoroughly dried in an oven and subsequently looked like ceramic powder. The X-ray diffraction pattern is presented in Figure 10. Mainly, phosphorus oxides were observed and various copper phosphates and copper phosphorus oxides were included in the by-product. It should be noted that the phosphate ions could be removed by oxidation at the cathode as well as by reaction with copper.

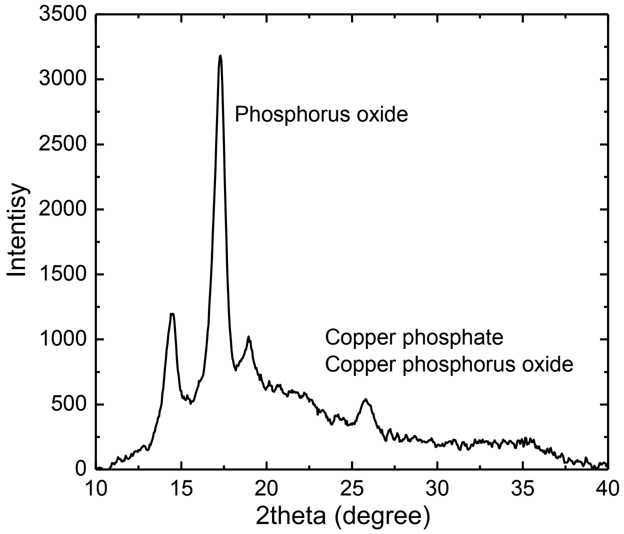


Figure 10. Result of X-ray photoelectron spectroscopy for sediment by electrolytic process with copper electrode in phosphate water solution

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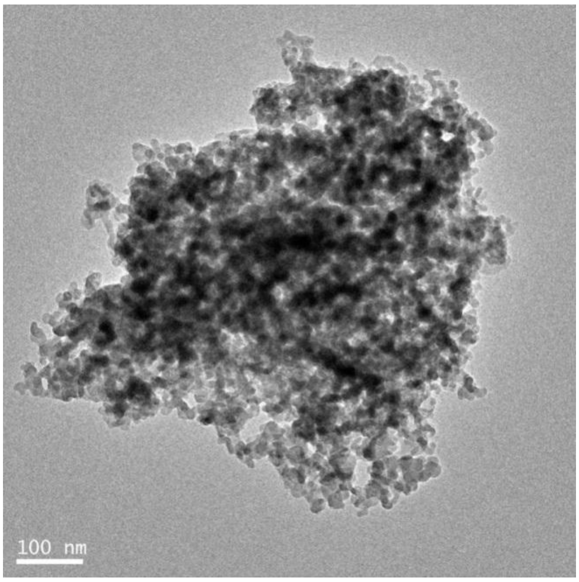

Figure 11. Micrograph of sediment by electrolytic process with copper electrode in phosphate water solution by transmission electron microscope

Figure 11 shows the microstructure of the by-product particle observed through transmission electron microscopy. The aggregated particle size was very large and non-uniform. However, the primary particle in the aggregated particle was very homogeneous and its size was around 10 nm. The particles were massively aggregated. The by-product primary particles might spontaneously aggregate in the solution with each other and grow to be a sufficiently large size for precipitation. Such inorganic particles can agglomerate very well in a base condition, so that the by-product particles can easily coagulate and precipitate as well.

Many researches have been performed about the electrochemical treatment wastewater. However, most studies were focused on the non-biodegradable organics removals by electro-Fenton or suspended solid by electro-coagulation.

According to the results of Kim and his co-authors [8], the electro phosphorus removal (EPR) process with aluminum plate electrodes was applied in a pilot-scale membrane bioreactor process, of which the phosphate removal was around 89.2%. The phosphate concentration in influent wastewater was 2.3mg/L and that of effluent was 0.3mg/L, respectively. Discharged Al^{+3} ions formed hard-to-dissolve precipitates of $AlPO_4$ in the presence of phosphate ions. Also, the phosphorus removal could be accomplished by an electrolysis process with titanium anode coated by IrO_2 and stainless cathode for swine wastewater [39]. They presented the result of the phosphate concentration variation from 83mg/L in influent wastewater to 15mg/L in effluent during a long retention time of 6 hours as their best performance. They did not discuss the mechanism for such results on the phosphate removal, while the phosphate ions would be oxidized at the anode to form the phosphorus oxide (P_2O_5) as discussed above and presented in Figure 10 in this paper. According to their results, the phosphate removal was strongly affected by the bias voltage variation; the removal efficiency was 3% at 3V, 21% at 5V, and 82% at 7V, respectively. It means that the phosphorus removal by only oxidation of phosphate would be strongly related to the applied voltage when the formation of phosphate compounds with metal anode is absent. Also, the retention time for the phosphate removal was too long as 6 hours for efficiency of 82%. In our study, most phosphate removal could be accomplished for less 0.5 h even at low voltage.

4. CONCLUSION

In this report, electrolysis operated constant voltage and low current conditions was performed, and the electrochemical experiment using three cathode materials such aluminum, iron, and copper to evaluate the removal characteristics of phosphate ion in wastewater. To estimate the stability of the copper electrode for a long time, the electrolysis experiments on synthetic wastewater with a higher concentration of 100mg/L were repeated 200 times for 10 minutes per each experiment under the bias voltage of 24V.

In case of the copper electrode couple, by-products with green blue color such as copper hydroxide ($Cu(OH)_2$) and copper phosphate ($Cu_3(PO_4)_2$) were formed on the surface of the anode and bubbles of hydrogen gas were formed on the surface of the cathode. The formation of copper hydroxide could contribute to removing phosphate because the hydroxyl ion (OH^-) in the copper hydroxide can be exchanged with the phosphate ion. The surface of the copper anode was relatively clean without oxidation, while the surfaces of the aluminum and iron anodes were completely changed from the initial state with severe oxidation. With such change to the anode surface such as aluminum and iron anodes, the electrolysis performance would degrade very fast. The corrosion of the surface would be also inhomogeneous and cause stress corrosion cracking, and the lifetime of the anode would not be guaranteed for a long period. In repeated electrolysis experiment using the copper electrode on synthetic wastewater with a higher concentration, the copper anode of 1mm thickness was sufficient to remove the phosphate which was more than 19g. The electrolysis with the copper electrode to remove phosphate was also stable for a long time.

ACKNOWLEDGEMENTS
This subject is supported by Korea Ministry of Environment as "Program for promoting commercialization of promising environmental technologies".

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