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Characteristics of Organics and Nutrients Removal in Municipal Wastewater Treatment by Electrolysis using Copper Electronic Conductor

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A novel electrolytic treatment process installed with copper electronic conductors was developed, and it was applied for the treatment of municipal wastewater under the conditions of constant voltage and adjustable current in a continuous mode. The organics could be successfully removed in very shorter reaction time through the electro-coagulation reaction. The fraction of copper hydroxide removed from the electronic conductor has been increased in the effluent as the electro-coagulation reaction progressed. The nitrogen could be reduced by the elimination of ammonia nitrogen, in early electrolysis reaction, and the phosphorus removal could be also accomplished by the formation of complicated compounds with metal such as copper phosphate. By the aeration after electrolysis reaction, the additional removal of organics by the oxidation and nitrogen by ammonia stripping could be achieved successfully. Thus, the electrolytic treatment process with copper electronic conductors would be good alternative method of conventional municipal wastewater treatment technologies for the simultaneous removal of organics and nutrients.

Keywords: Electrolysis, Electronic conductor, Municipal Wastewater, Organics, Nutrients

1. INTRODUCTION

Municipal wastewater is any water that has been adversely affected in quality by anthropogenic influence, and it comes from human waste, septic tank discharge, washing water, urban rainfall runoff, and so on [1]. When untreated municipal wastewater is discharged to water resources, it will lead to severe water pollution problems for aquatic life and nuisance conditions by the decomposition of the organic matters. In general, municipal wastewater contains high levels of the nutrients like nitrogen and phosphorus as well as organic matters. Excessive release of such wastewater can lead to a buildup of nutrients, called eutrophication, which can in turn encourage the overgrowth of weeds, algae, and cyanobacteria (blue-green algae). This may cause an algal bloom, a rapid growth in the population of algae. In addition to causing deoxygenation, some algal species produce toxins that contaminate drinking water supplies [1-3].

Most municipal wastewater have been treated by physical, chemical, and biological methods. The most well-known municipal wastewater treatment technology is the activated sludge process, based on the maintenance and recirculation of a complex biomass composed by micro-organisms [1,4]. However, only dissolved organic matters and colloids except nutrients such as nitrogen and phosphorus can be removed by the activated sludge process [5]. Thus, there is a growing need to introduce nutrient removal in municipal wastewater treatment, and many conventional biological treatment processes have been retrofitted for the nutrients removal. Numerous biological nutrient removal methods have been proposed and developed [4-7]. Nevertheless, the municipal wastewater treatment by application of biological nutrient removal process can be severely affected by many environmental and operating parameters, and especially the characteristics of influent wastewater. Neither biological removal of nitrogen nor phosphorus can be achieved without enough biodegradable organics [5-7]. Therefore, application of biological nutrient removal processes with biomass and nitrate recycle to the plants can cause serious problems such as insufficient removal and process stability.

Electrolytic treatment of municipal wastewater presents an alternative and innovative technology in which a sacrificial metal anode and cathode produce electrically active coagulants and tiny bubbles of hydrogen and oxygen in water [8]. Through the electrolysis reaction, effective removal of pollutants in municipal wastewater can be anticipated by strong oxidation, rapid treatment, easy operation, no limitation by influent fluctuation. Various electrolytic treatment have been developed to remove the pollutants in water and wastewater, such as electro-oxidation [9,10] and electro-coagulation [11-14].

However, existing electrolytic technologies for the treatment of wastewater have several disadvantages such as frequent replacement of the short life electronic conductor, over-consuming of electric power with no consideration on the wastewater concentration, and dangers such as electric shock accidents caused by operation under adjustable voltage and constant current conditions for the treatment of non-degradable organic wastewater with higher concentration [15]. A couple of metallic electronic conductors, a relatively stable cathode like titanium and a relatively active anode like iron or aluminum, were commonly used in most electrolytic technologies [16]. In our previous study [17,18], the copper electronic conductors have many advantages such as lower electronic conductor wearing and easier maintenance than other electronic conductors. In this study, a novel continuous flow electrolytic treatment process adopting copper electronic conductors and constant voltage and adjustable current conditions was developed and applied to the treatment of municipal wastewater. We have also conducted the evaluation of removal characteristics of organics and nutrients, and the settleability of by-product.

2. EXPERIMENTAL

The electrolytic treatment process comprised electrolysis reactor, pneumatic cleaning system, and power supply, as shown in Figure 1. The electrolysis reactor which made of plexiglass consists of three trains having a total liquid volume of 2L, and the trains were installed in parallel in the electrolysis reactor. Each train (40mmW×250mmL×1,200mmH) was piled up as cassettes, of which modules (40mmW×250mmL×50mmH) were stacked with twenty floors. Each floor had three electronic conductors (2mmW×190mmL×10mmH) array which was composed of two anodes at both sides of the cathode and a cathode at the center part.

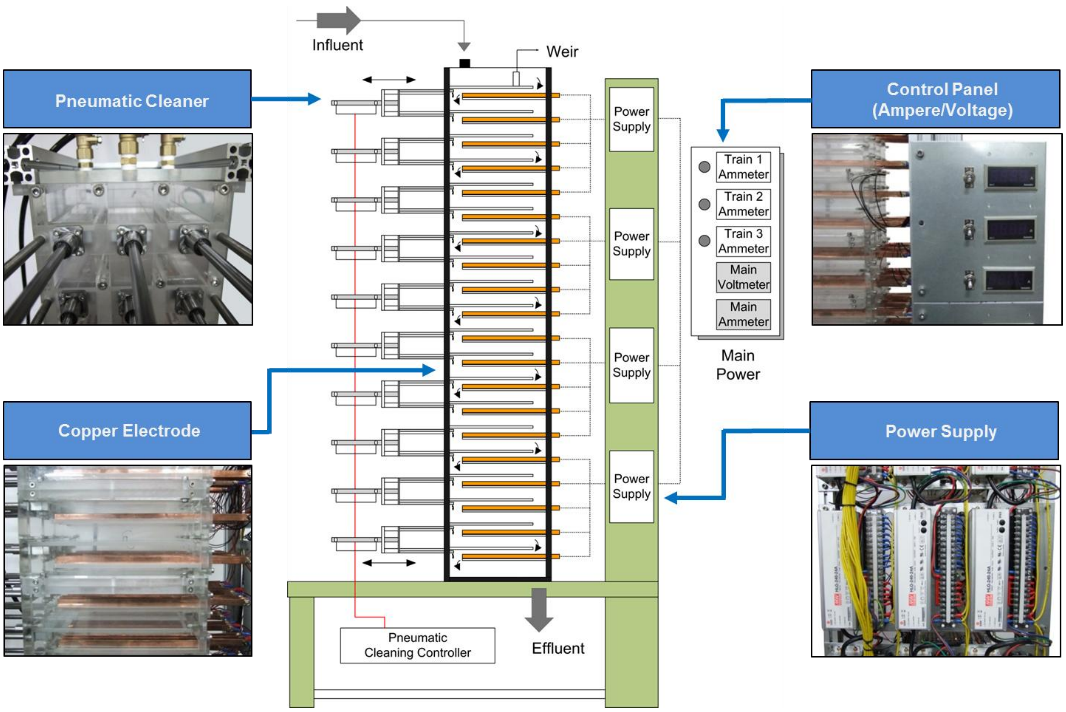

Figure 1. Schematic diagram of electrolytic treatment process

The electronic conductor cleaning system, which is one of the main part of electrolytic process, undertook a scraping with a brush for all cassettes. It was also driven by pneumatic power using nitrogen gas. The electrolytic treatment process was operated under constant voltage of 24 volts (V) and variable current with an upper limit of 10 amperes (A). A total of twelve power supply were utilized in the process and each power supplies supported various currents directly under the voltage of 24V for one module. During the electrolysis reaction, the real-time measurement of current value between the cathode and anode was performed. Influent municipal wastewater supply into the process was accomplished by a fluid pump (IPX8/KSP-2500, G-Electronics), and introduced between the electronic conductors on the floor into the first train of the electrolysis reactor. The effluent treated in the first train was also introduced subsequently in the second train, and then the effluent treated in the second train was finally handled in the third train. The electrolytic reaction time for each train was around 1.5 minutes and the wastewater was mixed to prevent the sedimentation of by-products in overall steps.

Influent was sampled from the end of the screen in a plant for the treatment of wastewater originated from small-communities located at Yeongwol in Korea. The general concentrations of organics such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the municipal wastewater ranged between 25~27.5 mg/L (average 27 mg/L) and 152~200 mg/L (average 177 mg/L), respectively. The concentrations of nutrients such as total nitrogen (TN) and total phosphorus (TP) were also 20.1~26.3 mg/L (average 23.2 mg/L) and 2.3~2.7 mg/L (average 2.5 mg/L), respectively. The influent was typical of municipal wastewater generated in Korea. All analyses were conducted as per procedures in the American Public Health Association (APHA) Standard Methods [19]. The COD was determined by the closed reflux method, and soluble BOD and COD were also measured after filtration of the sample using a glass-fiber filter. After the electrolysis experiment, the thermal characteristics and microstructure of the by-products were also examined by thermo gravimetric analysis (TGA, SHIMADZU, DTG-60H).

3. RESULTS AND DISCUSSION

The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in wastewater. BOD is the amount of dissolved oxygen needed by aerobic biological organisms in a water body to break down organic material present in a given water sample at certain temperature over a specific time period. BOD is similar in function to chemical oxygen demand (COD), in that both measure the amount of organic compounds in water and wastewater [20]. In this study, the analyses of COD and BOD were performed to evaluate the organics removal characteristics by the electrolytic treatment process. The concentration profiles of COD and BOD during the electrolysis are presented in Figure 2.

The initial concentrations of total COD and BOD in wastewater were around 200mg/L and 27mg/L, respectively. However, total COD and BOD were remarkably removed in very shorter reaction time of 2 minutes during the electrolysis, as shown in Figure 2. Whereas, more reduction of soluble COD and BOD which denoted the dissolved organics were not observed than that of total COD and BOD, despite of extension of electrolysis time. From this result, it seems to be that organics removal in the electrolytic treatment process can be achieved by the electro-coagulation reaction. The electro-coagulation has been well known to be more effective for the COD removal than the conventional coagulation and sedimentation processes. Soluble metal electronic conductors were found to be very effective in comparison to insoluble electronic conductors such as carbon.

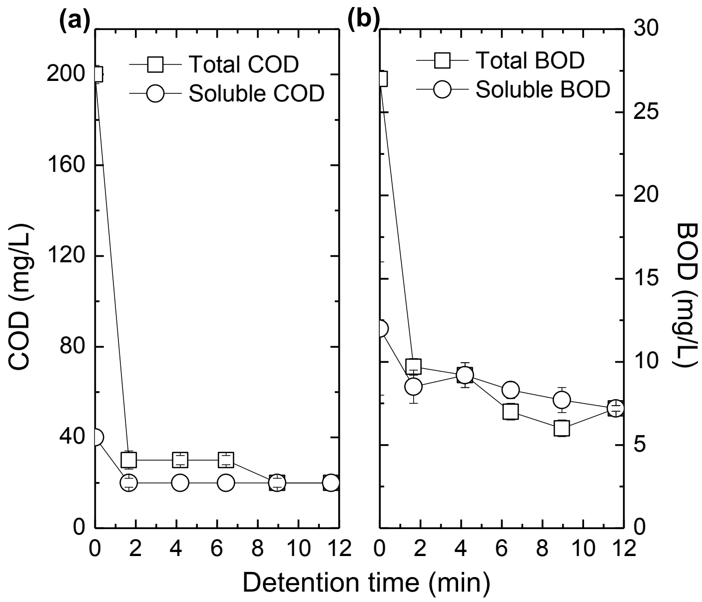

Figure 2. Concentration profiles of COD and BOD during the electrolysis ((a) COD profiles, (b) BOD profiles)

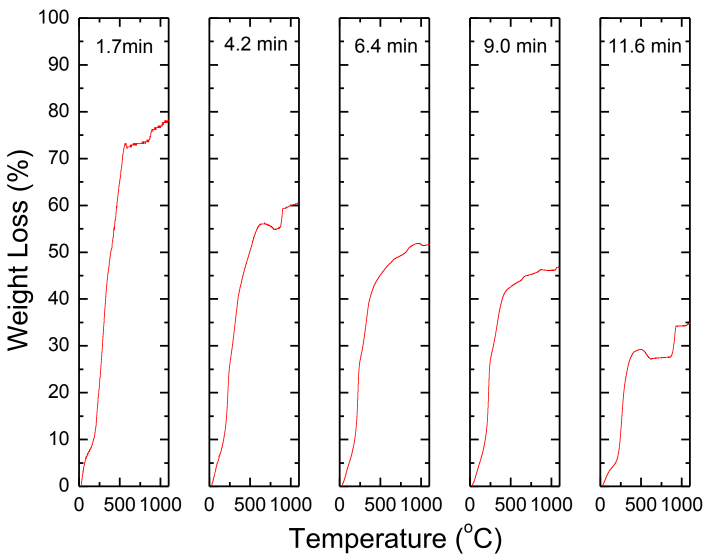

Figure 3. Results of TGA of by-product produced through the electro-coagulation

Figure 3 shows the results of thermo gravimetric analysis (TGA) of dried by-product generated through the electro-coagulation. As the electrolysis time increase, the weight loss of the by-product declined. The portion of organic pollutants in the by-product also reduced, because the pollutants removed by electro-coagulation reaction decreased gradually in the water. On the other hand, the by-product was produced consistently during the electrolysis procedure. Figure 4 shows the concentration of produced by-product and the variation of organic fraction in by-product through the electrolysis reaction, the suspended solids concentration increased continuously. However, volatile fraction in the suspended solids was changed in the range of 60mg/L and 90mg/L, the volatile fraction decreased gradually as the electrolysis reaction progressed. This means the fraction of copper hydroxide ($Cu(OH)_2$) removed from the electronic conductor increases in the effluent by electro-coagulation reaction.

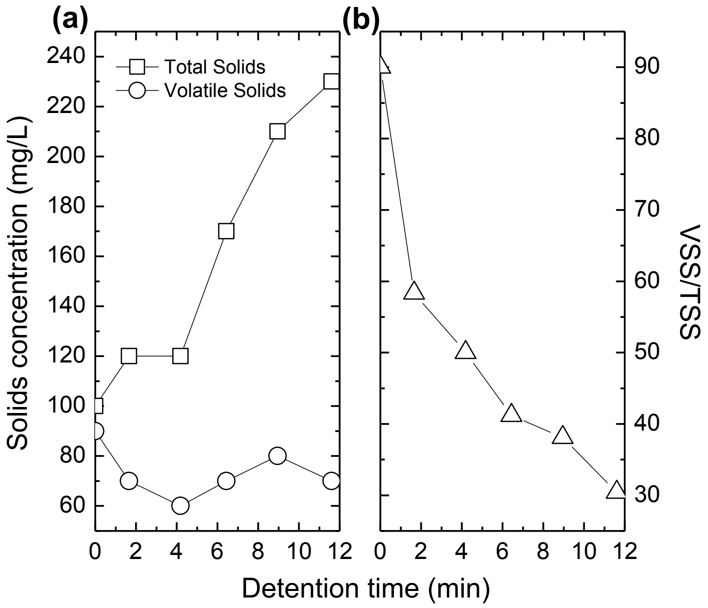

Figure 4. Concentration profiles of suspended solids during the electrolysis ((a) Solids Concentration, (b) VSS to TSS ratio)

The concentration profiles of nitrogen compounds during the electrolysis are demonstrated in Figure 5. The total nitrogen concentration decreased significantly in the beginning of electrolysis, and it caused by the elimination of ammonia nitrogen, which is a major component of most nitrogen in wastewater. Monica et al. [21] in 1980 reported that, by means of electrochemical process, ammonia could be effectively removed along with organic pollutants from the domestic wastewater mixed with seawater. Since then, electrochemical process has been successfully used for the removal of ammonia in wastewaters. The ammonia removal by electro-oxidation includes generally both direct and indirect oxidation reactions [22]. A direct oxidation of ammonia at electronic conductor–liquid interfaces of the anode was observed with the assistance of differential electrochemical mass spectrometry [23-25].

However, the removal of ammonia also takes place through an indirect oxidation route by both hydroxyl radicals and hypochlorous acid (HOCl) formed in electrochemical processes [5,6]. The hypochlorous acid reacts with the ammonium ion, and finally the ammonium ion can be stripped into nitrogen gas. As shown in Figure 5, the nitrate (NO_3^-) concentration increased slightly by the formation of nitrate through the reaction between ammonium ion and hypochlorous acid.

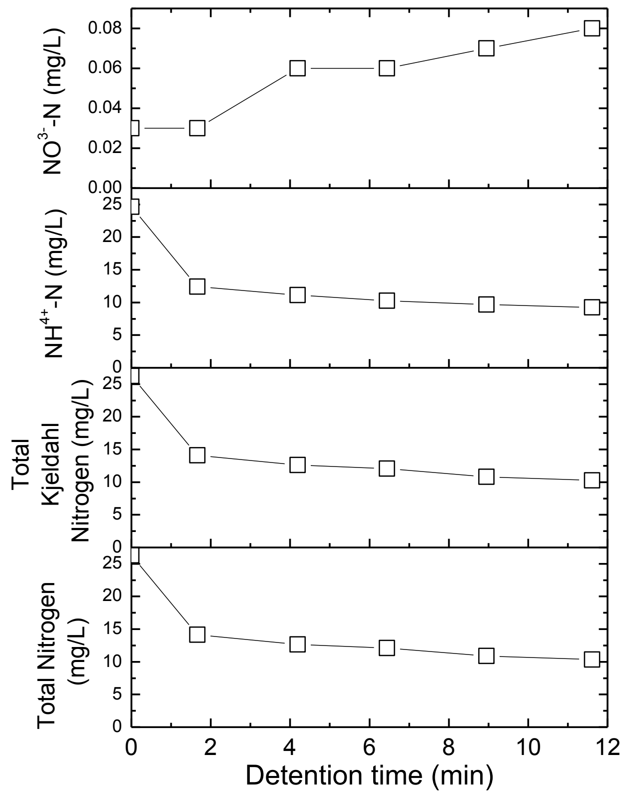

Figure 5. Concentration profiles of nitrogen compounds during the electrolysis

The concentration profiles of total phosphorus and orthophosphate during the electrolysis are illustrated in Figure 6. The phosphorus removal could be accomplished significantly in a very shorter reaction time within 2 minutes by the formation of complicated compounds with metal such as copper phosphate ($Cu_3(PO_4)_2$) during the electrolytic reaction. From the Result of X-ray photoelectron spectroscopy, in previous study [18], the copper phosphate having green blue color was observed actually in by-product by electrolysis with copper electrode in phosphate water solution. Phosphorus removal can be more efficient than that of nitrogen for the prevention of algal bloom, because the phosphorus concentration is generally lower than that of nitrogen in municipal wastewater. Thus, this electrolytic treatment process using the copper electronic conductor would be an good alternative to conventional biological phosphorus removal methods.

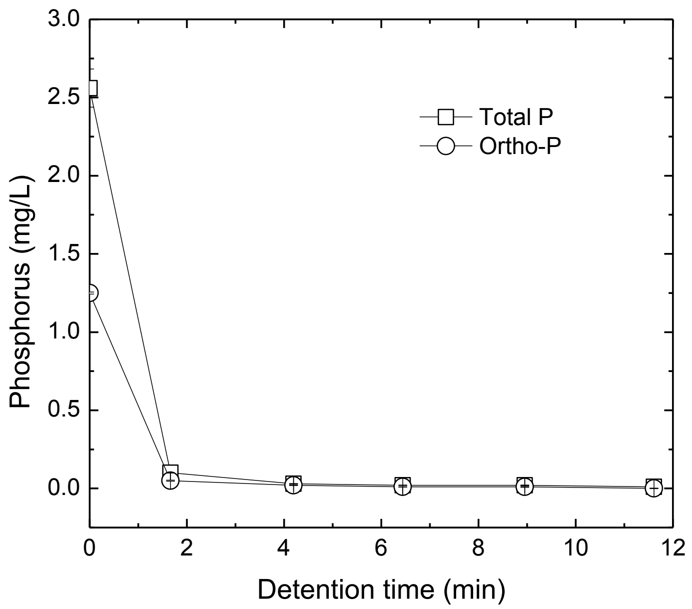

Figure 6. Concentration profiles of phosphorus during the electrolysis

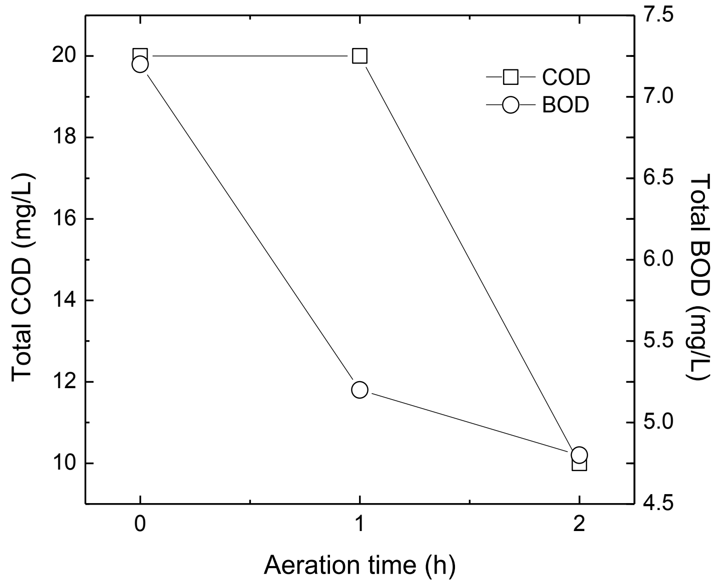

Figure 7. Changes of COD and BOD by additional aeration

As presented above, high removal of organics such as COD and BOD could be achieved in a very short reaction time of two minutes by electro-coagulation. However, in this study, the additional aeration was conducted for the enhanced organics removal, and its result was shown in Figure 7. The organics were removed successfully to the range of guaranteeing the effluent criteria for the preservation of water resources, as illustrated in Figure 7, and we could confirmed that the additional aeration after electrochemical procedure would be another method for the additional organics removal.

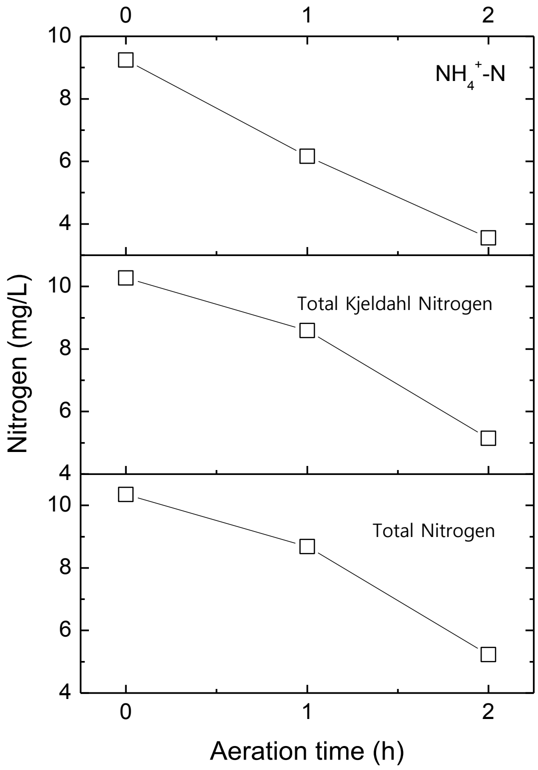

Figure 8. Changes of nitrogen by additional aeration

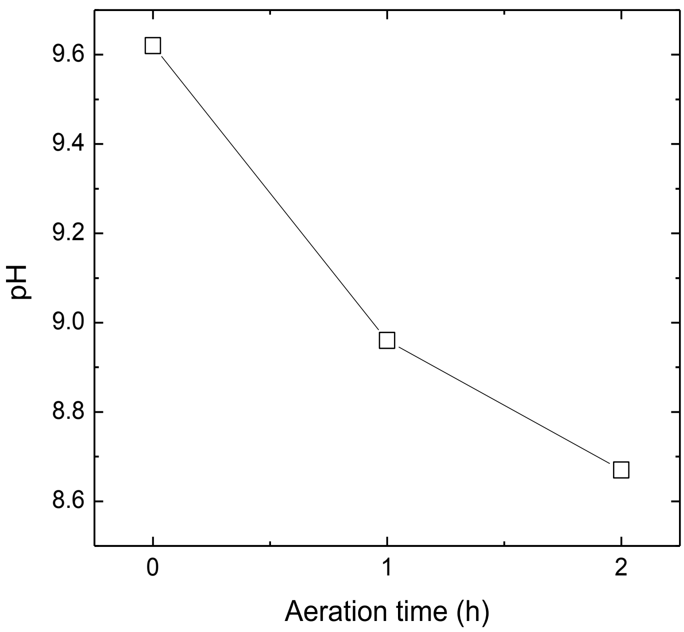

Figure 9. pH Change by additional aeration

The ammonia removal, which was the major component of total nitrogen removal, could be performed by extended aeration, as presented in Figure 8. Generally, ammonia reacts with water to form ammonium hydroxide (NH_4^+). Ammonia stripping is well known as a simple desorption process used to lower to ammonia content of wastewater. In ammonia stripping, lime or caustic is added to the wastewater until the pH reaches 10.8 to 11.5 standard units which converts ammonium hydroxide ions to ammonia gas (NH_3) [7]. The pH value increased to about 9.6 rapidly through the electrolytic reaction as shown in Figure 9, in this study, the free ammonium can be stripped successfully to the form of ammonia gas and the concentration of hydroxyl ion decreases.

4. CONCLUSION

In this report, by using of a novel continuous flow electrolytic treatment process with copper electronic conductors under the conditions of constant voltage and adjustable current, we have performed its application for the treatment of municipal wastewater. The organics in municipal wastewater could be noticeably removed in very shorter reaction time of 2 minutes by electro-coagulation reaction during the electrolysis. The portion of organic pollutants in the by-product also reduced, because the pollutants removed by electro-coagulation reaction decreased gradually in the water. The fraction of copper hydroxide ($Cu(OH)_2$) removed from the electronic conductor has been increased in the effluent as the electro-coagulation reaction.

The total nitrogen removal could be achieved in the beginning of electrolysis by the elimination of ammonia nitrogen. The phosphorus removal could be also accomplished significantly in a very shorter reaction time by the formation of complicated compounds with metal such as copper phosphate ($Cu_3(PO_4)_2$) during the electrolytic reaction. The extended aeration after electrochemical procedure was conducted for the enhanced organics removal, and we could found that the additional organics removal could be achieved as well as nitrogen removal by ammonia stripping.

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