Treatment of Waste Seawater by Electrolysis Using Charcoal Electrodes

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***Abstract*- Dissolved inorganic nitrogen is one of the major sources for eutrophication of lakes and coastal seas. Electrolysis is one of the expected tools for treatment of waste water. If metallic electrodes are used, the metal ions diffuse into water in the prolonged use. It costs too much to use platinum or gold for electrodes, which are difficult to diffuse into water. In the present study, carbon was proposed for the material of electrodes to decompose dissolved inorganic nitrogen in seawater. Among several kinds of carbons, active carbon was selected since diamond and graphite are expensive. Time variability of dissolved inorganic nitrogen was monitored in waste seawater to investigate the effects of electrolysis on decomposition of dissolved inorganic nitrogen. The seawater with the salinity level of about 3% was produced artificially. Ammonium was added to the water until its concentration was a few mg/L. The distance between the electrodes was 15 mm. Voltage was set to be 4V. As a result, ammonium, nitrite, and nitrate were decomposed successfully in the case of direct electric current power. The rates of decomposition of ammonium, nitrite, and nitrate were 2 mg/day, 2 mg/day, and 6 mg/day, respectively. However, the pH value increased since the hypochlorite was generated between the anode and cathode. The rate of decomposition of ammonium may be overestimated since the ammonium is converted into ammonia if the pH value increases. In the case of the alternating electric current, the pH value was able to be stabilized, however the rate of decomposition of dissolved inorganic nitrogen decreased. As future studies, it is indispensable to carry out the experiments that change the pulse width in a wider range. In addition, the concentrations of substances in the seawater should be monitored more precisely. Then the electrolysis system will be applied to marine aquaculture site for feasibility test, in comparison with the existing methods such as aeration.**

I. INTRODUCTION

Enhanced nutrients loadings from houses, industries, and agricultural lands cause eutrophication problems of lakes and coastal waters [1]. Eutrophication is characterized by increased algal growth, with hypoxia and anoxia events around water bottom. Nutrients loadings should be reduced by sewage disposal to abate eutrophication. The general sewage treatment system consists of primary, secondary, and tertiary treatments [2]. In primary treatment, solids are intercepted by screens. In second treatment, organic compounds are stirred in aerobic tanks so that they are decomposed into inorganic matters such as phosphate and ammonium. In tertiary treatment, dissolved phosphate is removed by combining with iron. Anaerobic tanks enable the removal of dissolved nitrogen by means of denitrification. However the tertiary treatment system is hardly prevailing since the system is quite expensive.

Electrolysis is one of the expected tools for treatment of waste water [3]. For example, the electrolysis is suitable for the small-scale sewage disposal system for each house. Fig. 1 shows the concept of energy supply and treatment of waste water for each house by using electrolysis. The electrolysis will be conducted by using power supplied from solar cell modules. In the electrolysis of the waste water, hydrogen is produced and accumulated into fuel cells for energy use. At the same time, organic wastes are decomposed by injecting oxygen and are converted into dissolved inorganic phosphorus nitrogen such as ammonium, nitrite, and nitrate. Then the dissolved inorganic nitrogen is decomposed directly into nitrogen gas by the electrolysis. The other example of the application of electrolysis is treatment of seawater in aquaculture [4]. Figure 2 shows a concept of treatment of waste seawater in the shrimp culture pond. In the intensive aquaculture, the sufficient amount of compounded food is given to the cultured shrimps and their excretions include high concentrations of dissolved inorganic nitrogen such as ammonium. Waste seawater from the aquaculture site should be treated to preserve the surrounding aquatic environment. The concentrations of dissolved inorganic nitrogen should be suppressed under the standard levels by means of biological and electrochemical techniques. Electrolysis will be quite useful to decompose

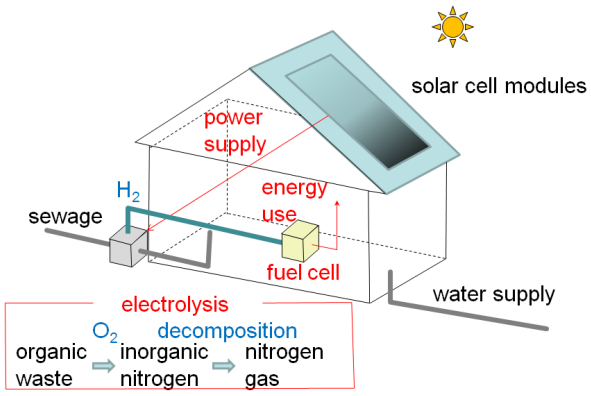

Figure 1: A proposed system of energy supply and treatment of waste freshwater by means of electrolysis for a general house.

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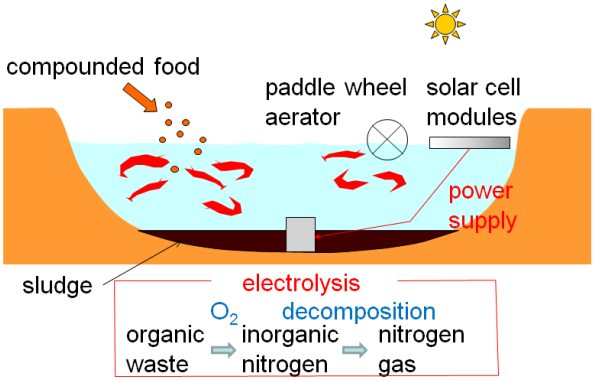

Figure 2: A proposed system of treatment of waste seawater by means of electrolysis for the culture of shrimps.

sludge into dissolved inorganic nitrogen and to remove the dissolved inorganic nitrogen directly.

Electrolysis has been paid to attention as a new method of processing waste water. A lot of studies have been carried out by researchers [3-11]. The general electrodes are produced by metals such as platinum to prevent the ionization of metals into waters. The electrodes made by diamond are tried for electrolysis of waste water. However, such electrodes are quite expensive for practical use and may be consumed by ionization under a high voltage for prolonged use. The ionized metals may be accumulated in aquatic lives as toxic elements.

In the present study, active carbon or charcoal are used for electrodes. Electrolysis is executed for seawater and the removal of dissolved inorganic nitrogen is examined.

II. METHOD

A. *Preliminary Experiment*

In the preliminary experiment, graphite electrodes were soaked directly into the freshwater in an acrylic water tank. Electrolysis was carried out for three days. Figure 3 shows the pictures of the water at the beginning of the experiment and after three days from the beginning of the experiment. As a result, the water changed color into black after three days, while the water was transparent at the beginning of the experiment. The black powder was examined by filtering the discolored water. It turned out that the black powder was carbon particles which have conductivity. The same phenomenon was observed for the other electrodes such as charcoal. In order to use the electrodes in the actual water, the carbon particles should be enclosed in the electrodes.

B. *Development of New Electrodes*

Figure 4 shows new electrodes in which the active carbon is separated from the seawater. The active carbon is enclosed by acrylic board and the filters made of alumina. The filters do not

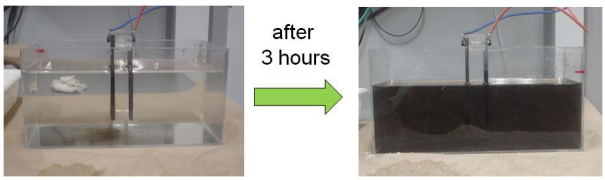

Figure 3: Preliminary experiment of electrolysis by means of graphite electrodes in freshwater.

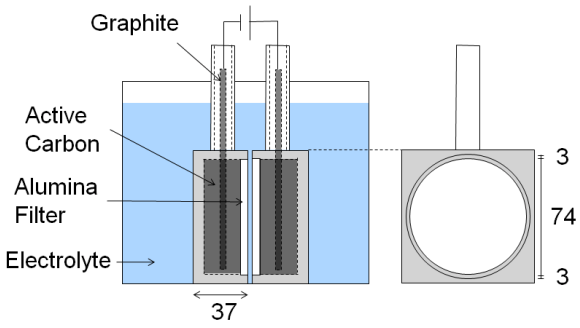

Figure 4: New electrodes in which charcoal is enclosed by acrylic boards and alumina filter.

pass the particulate carbons but pass the ions. Graphite is used in the joint between active carbon and power supply.

C. *Experimental Conditions*

Waste water was made by breeding the aquatic life. The old active carbons were used for the materials of electrodes since new active carbons have a function of absorbing dissolved inorganic nitrogen. The salinity was adjusted artificially to 3% by adding salt. Ammonium was added to the water until its concentration was a few mg/L. The volume of the seawater was 5 L. The distance between the electrodes was 15 mm.

First, waste seawater was decomposed by electrolysis in the condition of direct current power. Voltage were set to be 4 V. The intensity of an electric current was around 0.5 A at the beginning of the experiment. Then alternating current was used to suppress the production of chlorine and hypochlorous acid. The pulse width of the alternating current was set to be 0.01, 0.02, 0.08, 0.20, and 0.55 seconds.

In order to examine the decomposition of dissolved inorganic nitrogen, the concentrations of ammonium, nitrite, and nitrate were monitored by Pack Test (Kyoritsu Chemical-Check Laboratory Corporation) 3-5 times a day. The value of pH was monitored by a pH meter at the same time.

III. RESULTS AND DISCUSSIONS

Figure 5 shows the time variability of ammonium, nitrite, nitrate, and the pH when direct current power was used. At the beginning of the experiment, the concentration of ammonium

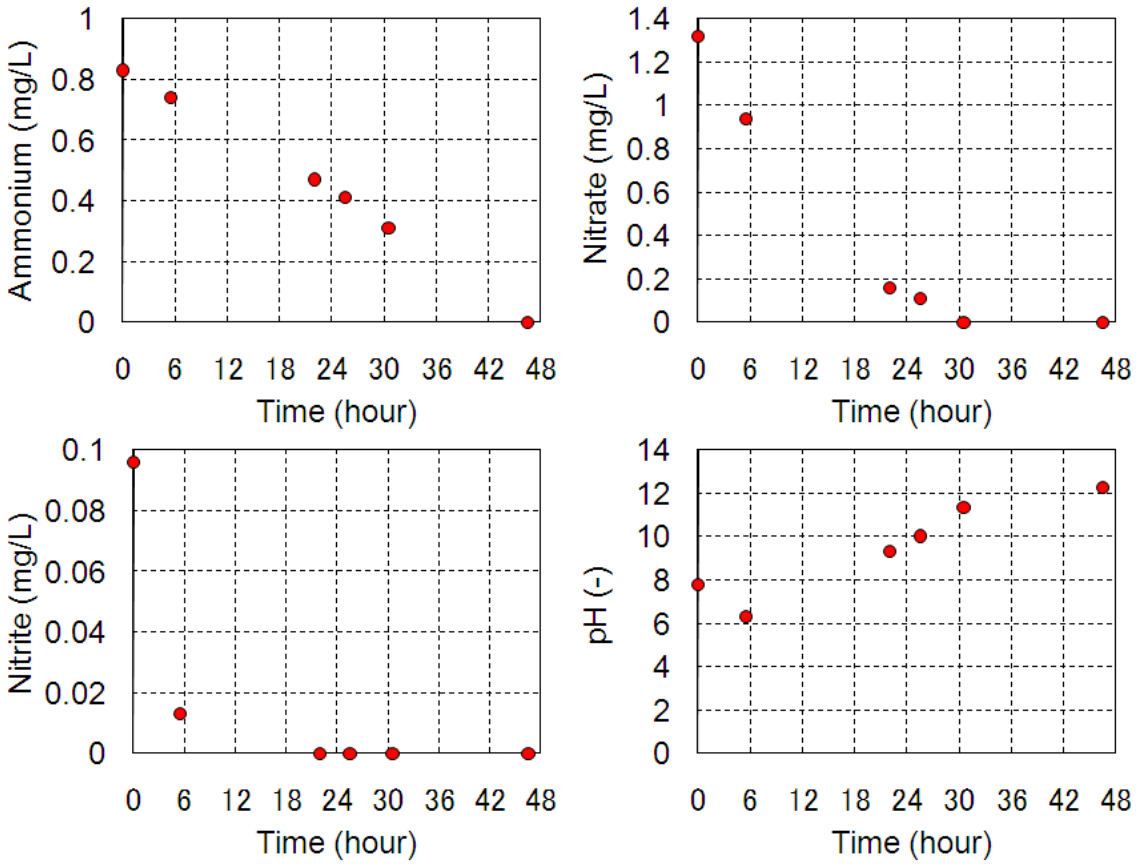

Figure 5: Time variability of ammonium, nitrite, nitrate, and pH during 2 days of experiment in the case of direct electric current.

was around 0.8 mg/L, and then it decreased linearly to almost 0 mg/L after two days from the beginning of the experiment. The concentration of nitrite decreased from 0.1 mg/L to 0.015 mg/L after six hours from the beginning of the experiment. The concentration of nitrate decreased from 1.3 mg/L to less than 0.2 mg/L after a day from the beginning of the experiment. The concentrations of dissolved inorganic nitrogen decreased linearly when the levels of concentrations were high, while the rate of decomposition decreased as the concentrations of dissolved inorganic nitrogen decreased. The rate of decomposition was calculated as 2 mg/L, 2 mg/L, and 6 mg/L for ammonium, nitrite, and nitrate, respectively. The following reactions were assumed to take place at the anode, the seawater between the anode and cathode, the cathode as a mechanism that the concentrations of ammonium, nitrite, and nitrate.

[At the anode]

$2Cl^- \rightarrow Cl_2 + 2e^-$ (1)

$Cl_2 + 3H_2O \rightarrow 2HClO + 3H^+ + OH^-$ (2)

[Between the anode and cathode]

$HClO + NH_2CL \rightarrow NHCl_2 + H_2O$ (3)

$NHCl_2 + H_2O \rightarrow NOH + 2HCl$ (4)

$NHCl_2 + NOH \rightarrow N_2 + HClO + HCl$ (5)

[At the cathode]

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

$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$ (7)

According to the above reactions, the hypochlorite is generated between the anode and cathode. The PH value increased from 8 to 12 at the end of the experiment. This is because the generation of the hypochlorite made seawater alkalinity. Ammonium is generally converted into ammonia under the condition of alkalinity, so the rate of decomposition of ammonium may be overestimated.

Figure 6 shows the time variability of the concentrations of ammonium, nitrite, nitrate, and pH when the pulse width of the alternating electric current was 0.01s. The change in the pH value was stabilized by using the alternating electric current. The concentration of ammonium decreased a little, while the concentrations of nitrite and nitrate increased. Therefore the rate of decomposition of dissolved inorganic nitrogen was reduced in the case of the alternating electric current. Table 1 summarizes the changes in the concentrations of ammonium, nitrite, nitrate, and pH when the pulse width of the alternating electric currents were set to be 0.01 s, 0.02 s, 0.08 s, 0.20 s, and 0.55 s. It was expected that the rate of decomposition of dissolved inorganic nitrogen approaches the result when direct current was used as the increase in the pulse width. However,

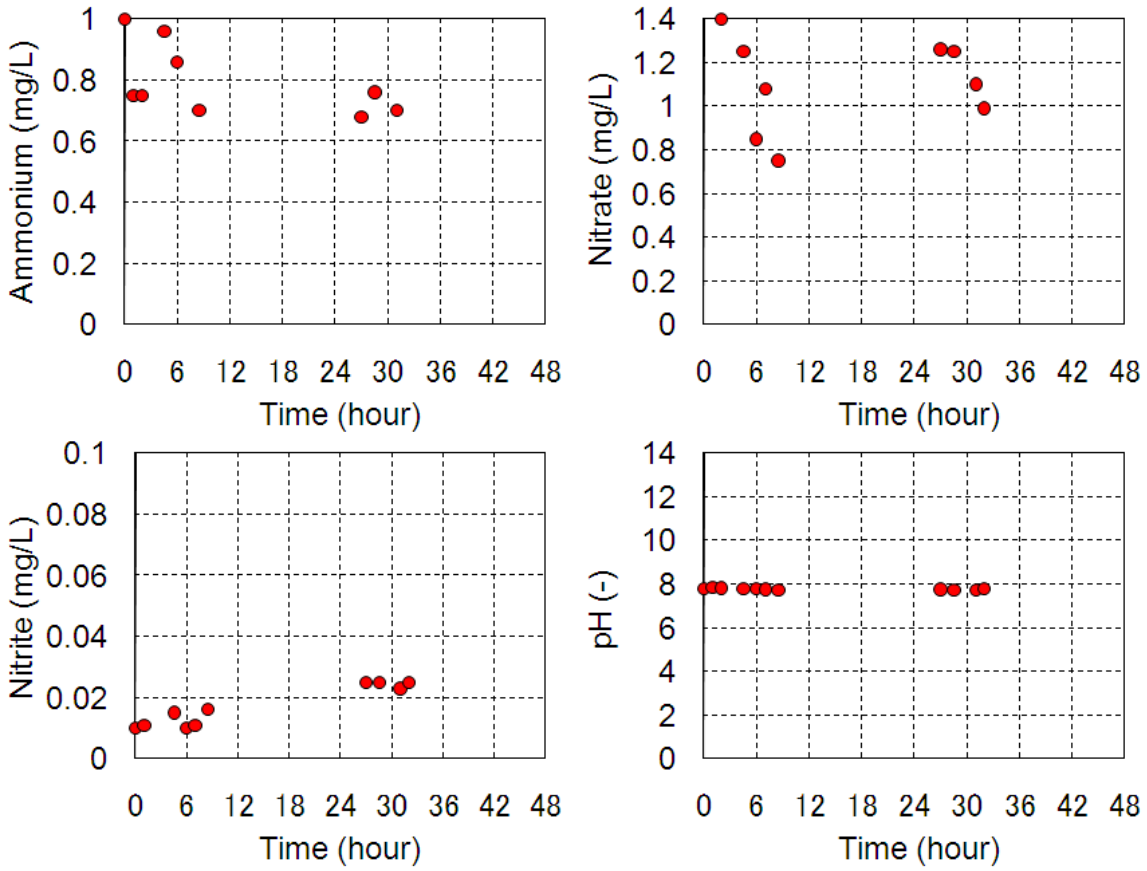

Figure 6: Time variability of ammonium, nitrite, nitrate, and pH during 2 days of experiment in the case of alternating electric current with the pulse width of 0.01 s.

the difference in the characteristic of decomposition rate caused by pulse width was hardly observed in the present experiments. Consequently, the rate of decomposition of dissolved inorganic nitrogen became smaller in the case of the alternating electric current though the pH value was able to be stabilized. As future studies, it is indispensable to carry out the experiments that change the pulse width in a wider range.

IV. CONCLUDING REMARKS

In the present study, the experiments of decomposition of dissolved inorganic nitrogen were carried out using the electrodes made of the active carbon. If carbon was installed directly into the water in the experiment of electrolysis, the water was discolored to the black since the carbon electrodes became small particles. In order to prevent the leak of carbon particles, the active carbon was enclosed by acrylic boards and alumina filters. In the case of direct electric current power, ammonium, nitrite, and nitrate were decomposed successfully. The rates of decomposition of ammonium, nitrite, and nitrate were 2 mg/day, 2 mg/day, and 6 mg/day, respectively. However, the pH value increased since the hypochlorite was generated between the anode and cathode. The rate of decomposition of ammonium may be overestimated since the ammonium is converted into ammonia if the pH value increases. In the case of the alternating electric current, the pH value was able to be stabilized, however the rate of decomposition of dissolved inorganic nitrogen decreased. As future studies, it is indispensable to carry out the experiments that change the pulse width in a wider range. In addition, the concentrations of substances in the seawater should be monitored more precisely. Then the electrolysis system will be applied to marine aquaculture site for feasibility test, in comparison with the existing methods such as aeration.

TABLE I
THE CHANGES IN THE CONCENTRATIONS OF AMMONIUM, NITRITE, NITRATE, AND PH WHEN THE PULSE WIDTH OF THE ALTERNATING ELECTRIC CURRENTS WERE SET TO BE 0.01 S, 0.02 S, 0.08 S, 0.20 S, AND 0.55 S.

Pulse Width [s]	Ammonium [mg/day]	Nitrite [mg/day]	Nitrate [mg/day]	pH [-]
0.01	0.55	-0.055	-0.325	-0.01
0.02	0.1	-0.02	-1.85	-0.05
0.08	-0.7	-0.0225	0.325	0.04
0.20	0.3	-0.0375	0.025	0
0.55	0.35	-0.0075	n.d.	-0.06

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