RESEARCH ARTICLE

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Electrochemical Treatment of Wastewater Containing High Concentration of Ammonia

Ratnawati Ratnawati*, Putri Pratiwi, and Ni Putu Wedha Ramanitya*

Department of Chemical Engineering, Diponegoro University, Semarang 50275, Indonesia

Fertilizer industry wastewater may contain high concentration of ammonia up to 3000 mg NH_3-N/L. Electrolysis is a promising method for treating such wastewater by converting ammonia to eco-friendly products, i.e., hydrogen and nitrogen. This work was aimed to study the effect of initial concentration of ammonia, current density, and electrode materials on the electrolysis of synthetic wastewater containing high concentration of ammonia. The experiment was conducted by varying ammonia concentration (585–1555 mg NH_3-N/L), current density (20–40 mA/cm^2), electrode material (anode: Cu; cathode: Al, Zn, Fe), and time (0–20 minutes). The results show that higher initial concentration of ammonia results in smaller conversion of ammonia to hydrogen. On the other hand, as the current density rises, the electrolytic reaction occurs more rapidly. Electrolysis using cathode Al is able to convert ammonia to hydrogen better than the other electrodes are.

Keywords: Ammonia, Electrolysis, Hydrogen.

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1. INTRODUCTION

Wastewater from fertilizer and petrochemical industries, piggery wastewater, and landfill leachate may contain up to 3000 mg NH_3-N/L.[1] This wastewater cannot be dumped to the aquatic environments as high concentration of ammonia is toxic to a wide range of aquatic organisms, especially fish.[2] All marine fish species will suffer growth disturbances at ammonia level higher than 0.11 mg NH_3-N/L.[3]

Various methods have been used to remove ammonia from wastewater, including biological nitrification, air-stripping, and ion exchange. It was found out that none of these methods have been entirely satisfactory as expected.[4] By using anaerobic microorganism, ammonia can be degraded through oxidation. However, this process produces soluble nitrate and nitrogen oxides which are toxic to aquatic organisms. Both biological and air-stripping methods are not able to lower the concentration of ammonia to the level required in the waste water quality standards. Ion exchange method is able to decrease the concentration of ammonia to a very low level, however, it needs high cost and it basically transfers ammonia from one medium to another.[5]

Recently, the electrochemical method has attracted for the treatment of wastewater containing ammonia.[6–10] By this method, ammonia is converted to hydrogen and nitrogen. The reactions taking place in the electrolysis cell are:

$$NH_{3(l)} + 6OH^-_{(aq)} \rightarrow N_{2(g)} + 6H_2O_{(l)} + 6e^- \quad \text{with } E^0 = -0.77 \text{ V/SHE}$$

$$6H_2O_{(l)} + 6e^- \rightarrow 3H_{2(g)} + 6OH^-_{(aq)} \quad \text{with } E^0 = -0.82 \text{ V/SHE}$$

The first and the second reactions take place at the anode and the cathode of the electrolytic cell, respectively. E^0 is the standard electrode potential. The overall reaction is

$$NH_{3(l)} \rightarrow N_{2(g)} + 3H_{2(g)} \quad \text{with } E^0 = -0.059 \text{ V/SHE}$$

Hydrogen and nitrogen gases are nontoxic and furthermore, hydrogen is considered as the cleanest fuel with enormous heat of combustion. It means that electrochemical oxidation of ammonia may solve environmental problem caused by ammonia and at the same time produce energy.[11]

Electrolysis is influenced by various factors, such as types of electrodes, current density, concentration of ammonia in the wastewater, and time. The aim of this work is to study the effect of those variables on the electrolysis of ammonia in wastewater.

2. EXPERIMENTAL DETAILS

The wastewater used in the experiment was a synthetic mixture prepared by diluting ammonia solution 25% (Merck Millipore Cat. No. 105432) to various concentrations (585 to 1555 mg NH_3-N/L). The experiments were run in batch mode at room temperature (28–32 °C) in an apparatus depicted in Figure 1. The electrolysis chamber (1) is equipped with electrodes (2), a sampling port (3), and gas outlet (4). The anode used in this work was copper, while the cathode (4) was varied (Al, Zn, Fe). The size of both anode and cathode was 20 mm × 50 mm × 1 mm, and the distance between them was 10 mm. Direct current power

*Authors to whom correspondence should be addressed.

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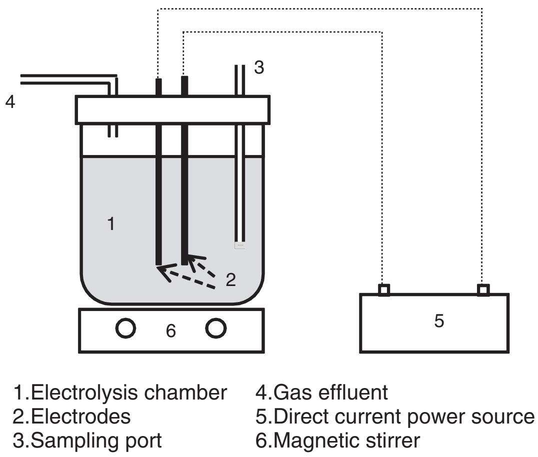

Fig. 1. Schematic experimental layout.

source (5) supplied the voltage of 4 V with various current densities (20–40 mA/cm^2). One thousand and five hundreds milliliter of ammonia solution was added into the electrolysis chamber (1). The solution was stirred using a magnetic stirrer (6) at constant stirring speed (200 rpm). Samples were periodically taken from the sampling port (3) in every 4 minutes for subsequent analysis of ammonia concentration. The concentration of ammonia was determined using Nessleration method according to ASTM D1426.

3. RESULTS AND DISCUSSION

3.1. Effect of Initial Concentration of Ammonia

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The effect of initial concentration of ammonia on electrolysis process using Cu as anode and Al as cathode with current density of 20 mA/cm^2 and voltage of 4 V is depicted in Figure 2. The remaining ammonia in the solutions are 20, 34.5, and 66.6 NH_3-N/L for initial concentration of 585, 1040, and 1555 mg NH_3-N/L, respectively. It means that the remaining ammonia is higher for higher initial concentration of ammonia. The same trend is also observed for electrolysis processes using Zn and Fe as anode with current density of 30 and 40 mA/cm^2.

The phenomenon can be related to the decreasing activity of electrodes during direct ammonia oxidation in aqueous media

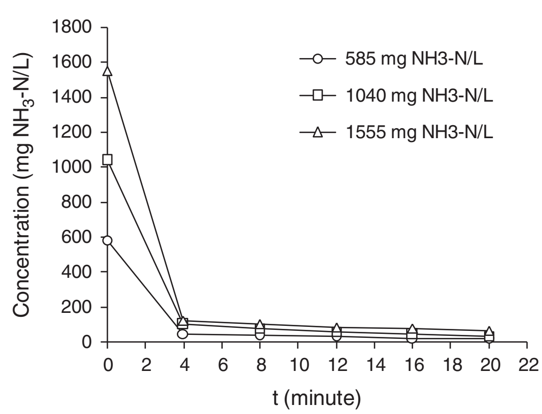

Fig. 2. Effect of initial concentration of ammonia on the remaining ammonia in the solution electrolyzed using Cu as anode and Al as cathode with voltage of 4 V and current density of 20 mA/cm^2.

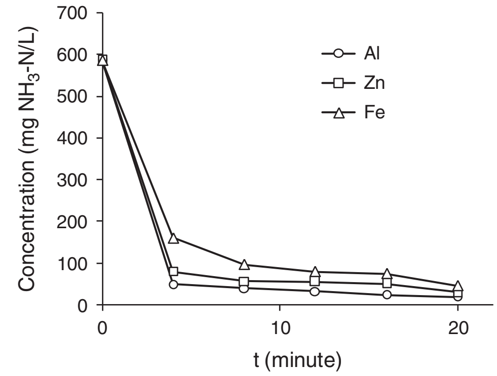

Fig. 3. Effect of cathode material on the concentration of ammonia in the solution electrolyzed using Cu as anode with initial ammonia concentration of 585 mg NH_3-N/L, voltage of 4 V, and current density of 20 mA/cm^2.

by adsorbed intermediate nitrogen species (NH_2, NH, N) formed during the oxidation.[2,12] The mechanism of Pt electrode surface poisoning was first proposed by Gerischer and Mauerer as the following reactions where x, $y = 1$ or 2.[13]

$$NH_{3,\,aq} \leftrightharpoons NH_{3,\,ads}$$

$$NH_{3,\,ads} \leftrightharpoons NH_{2,\,ads} + H^+ + e^-$$

$$NH_{2,\,ads} \leftrightharpoons NH_{ads} + H^+ + e^-$$

$$NH_{x,\,ads} + NH_{y,\,ads} \leftrightharpoons N_2 + (x+y)H^+ + (x+y)e^-$$

$$NH_{ads} \leftrightharpoons N_{ads} + H^+ + e^-$$

$$N_{ads} + N_{ads} \leftrightharpoons N_{2,\,ads}$$

$$N_{2,\,ads} \leftrightharpoons N_{2,\,aq}$$

The oxidation is initiated by adsorption of ammonia molecules on the surface of electrode. The adsorbed ammonia is then decomposes to yield adsorbed intermediates (NH_x) before the intermediates form molecular nitrogen through recombination. The same mechanism was also proposed for surface poisoning on transition metal electrodes with N_{ads} was identified as the surface poison.[14]

With higher initial concentration of ammonia, the more the amount of intermediate molecules, including N_{ads} formed on the electrode surface. These intermediates block the active sites of the electrode for ammonia adsorption.[15,16] This will further result in more remaining ammonia in the solution. Similar results were also reported for depositing electrolytic coatings of a nickel-molybdenum alloy.[17]

3.2. Effect of Cathode Material

The standard electrode potential (E^0) for Cu, Fe, Zn, and Al are 0.34, −0.41, −0.76, and −1.66 V, respectively. Among the

Table I. Final concentration of ammonia for different initial concentration and cathode material.

Initial concentration of ammonia (mg NH_3-N/L)	Conversion (%) by using electrode		
	Cu/Al	Cu/Zn	Cu/Fe
585	96.9	95.2	92.13
1040	96.7	94.9	91.83
1555	95.7	94.7	91.79

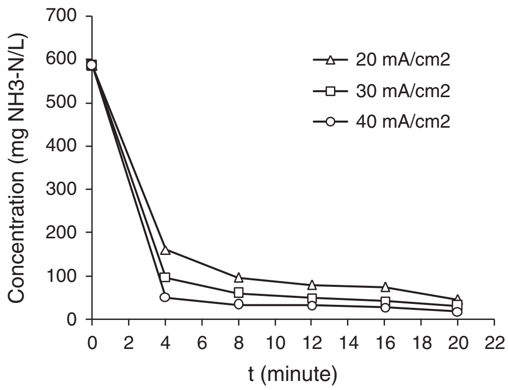

Fig. 4. Effect of current density on the concentration of ammonia in the solution electrolyzed using Cu as anode and Fe as cathode with initial ammonia concentration of 585 mg NH_3-N/L and voltage of 4 V.

four metals, Cu is the strongest oxidizing agent, while Al is the strongest reducing agent.[18] For this reason, Cu is used as the anode, while other metals are used as the cathode.

The effect of cathode material on electrolysis process using Cu as anode with initial concentration of ammonia of 585 mg NH_3-N/L, current density of 20 mA/cm^2, and voltage of 4 V is depicted in Figure 3. It is observed in the figure that as a cathode, Al is the most effective, followed by Zn and Fe. Similar results are also obtained in electrolysis with initial ammonia concentration of 1040 and 1555 mg NH_3-N/L. However, the percentage of ammonia electrolyzed is lower for higher initial ammonia concentration. The percentage of conversion of ammonia after 20 minutes of electrolysis with various initial ammonia concentrations using various cathodes are summarized in Table I. All results presented in Table I were obtained in electrolysis with current density of 20 mA/cm^2.

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According to Figure 3 and Table I, using Al as the cathode, the conversion of ammonia to hydrogen and nitrogen is the highest, followed by Zn and Fe. The difference between the standard electrode potential of the Cu and Al is greater than that of Cu and Zn, while the difference between Cu and Zn is greater than that of Cu and Fe. It makes Al is more effective than Zn and Fe as a cathode and gives higher conversion.[19]

3.3. Effect of Current Density

The effect of current density on the concentration of ammonia in the solution is depicted in Figure 4. The data were obtained using initial ammonia concentration of 585 mg NH_3-N/L, Cu as anode, Fe as cathode, and voltage of 4 V. It is seen in the figure that the concentration of ammonia remaining in the solution is lower as the current density becomes higher.

In electrochemical treatment of dye, current density is the most important parameter for controlling the reaction rate. The efficiency of color removal increases as the current density becomes higher.[20,21] Electrolytic transformation of benzene was reported to be occurred more rapidly as the current density applied was higher.[22]

4. CONCLUSION

Electrolysis of ammonia to yield hydrogen and nitrogen has been conducted. The electrolysis is influenced by the initial ammonia concentration, cathode material, and current density. Higher initial ammonia concentration results in lower conversion of ammonia. Al is more effective for cathode than Zn and Fe. Greater current density results in higher conversion of ammonia.

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