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## Contact Glow Discharge Electrolysis System for Treatment of Wastewater Containing Ammonia

Nelson Saksono, Bagus Priyogoreno Adiwidodo, Eva Fathul Karamah and Sutrasno Kartohardjono

Department of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia

*Corresponding Author: Sutrasno Kartohardjono, Department of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia*

### ABSTRACT

Contact glow discharge electrolysis produced many active species such as OH radical, which has important role in degrading complex pollutants. This study utilizes Contact Glow Discharge Electrolysis (CGDE) system to remove ammonia from wastewater. Variables such as electrolyte concentration, voltage and temperature are studied their effects on CGDE's performance. Experimental results show that the hydroxyl radicals produced is higher than the ammonia degraded during the CGDE process. In general, increasing potential discharge will increase electrical current. The highest yield of hydroxyl radicals was obtained at a depth of anode 5 mm although the anode surface area more submerged than CDGE. Ammonia degradation efficiency increase with increases in electrolyte concentration, voltage and temperature applied in the CGDE processes. The optimum condition is achieved using KOH 0.02 M at 700 v and 60°C, where at such condition ammonia degradation efficiency and energy consumption are 89.2% and 80 kJ mmole<sup>-1</sup>, respectively. These results show that the CGDE process has the potential to be used to degrade wastewater containing ammonia.

**Key words:** Ammonia, degradation efficiency, energy consumption, hydroxyl radical and plasma

### INTRODUCTION

Water is a vital need for every living creatures and human being in particular. The need for clean water each year increased with increasing human population, so that more and more people who have trouble getting clean water today. This has caused contamination of various water sources such as rivers and lakes by various wastes resulting from human activity itself. One of these contaminants is ammonia. Ammonia is also produced from the urine which is the result of a reaction between uric acid and a little water in the secretion system of humans and animals. The presence of ammonia in water is very dangerous to aquatic life as it can kill fish and cause algae bloom because of nitrogen content in ammonia to fertilize plants in water (Zhang *et al.*, 2011).

Contact Glow Discharge Electrolysis (CGDE) is one of the advanced oxidation methods, which are very productive in generating hydroxyl radicals in which these hydroxyl radicals are non-selective reactive species that can degrade various components (Jin *et al.*, 2010). The hydroxyl radical is a powerful oxidant and is very effective to degrade several compounds in wastewater, which are difficult to oxidize such as acridine orange (Gao *et al.*, 2001). Gao *et al.* (2001) have reported that the conversion rate on plasma electrolysis wastewater containing acridine orange can

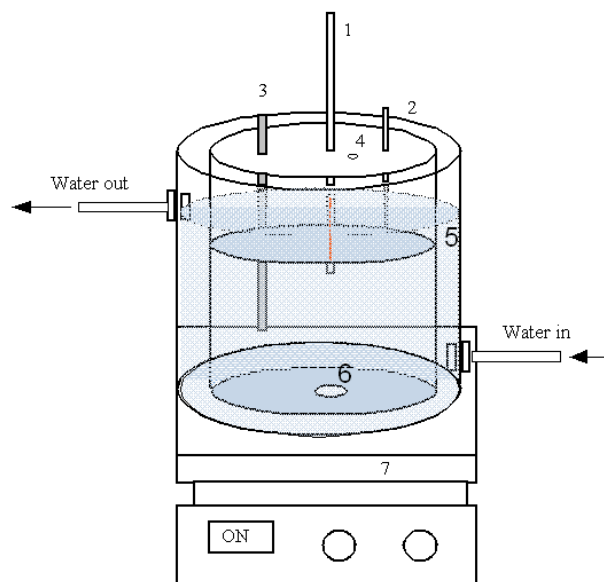


Fig. 1: Schematic diagram of CGDE reactor, 1: Thermometer, 2: Anode (wolfram), 3: Cathode (stainless steel), 4: Sample port, 5: Cooling jacket, 6: Magnetic stirrer and 7: Stirrer

reached approximately 90% at a voltage of 500 v. Meanwhile, Liu *et al.* (2010) has found that decomposition of nitrophenol in wastewater through plasma electrolysis produced nitrate ions in compounds and  $\text{CO}_2$ . The aim of this study is to see the effectiveness of CGDE process in degrading ammonia from wastewater based on ammonia degraded and energy consumption.

## MATERIALS AND METHODS

The experimental set-up is shown in Fig. 1 where CGDE is done in a batch reactor system surrounded by a cooling jacket using cooling water circulation. The anode is made of tungsten, which is only the tip contacted the surface of the solution. Meanwhile, the cathode is a cylindrical stainless steel dipped into solution. Operating conditions in the experiments are in the range of voltage and temperature of 500-700 v and 50-60°C, respectively. Meanwhile, the wastewater used in the experiments was made by diluting ammonium sulfate into potassium hydroxide solution of 0.01-0.03 M.

The parameters studied were the percentage of ammonia degradation and energy consumption (kJ) needed to degrade every mmole of ammonia. Ammonia contents in wastewater were measured using Nesslerization method in spectrophotometer beam UV-Visible double Hitachi 200-20. Meanwhile, hydrogen peroxide produced during CGDE processes were measured using iodometry titration (Liu *et al.*, 2010).

## RESULTS AND DISCUSSION

The results of this study are divided into two parts, namely the measurement of OH radical product and performance evaluation of plasma electrolysis reactor through several important parameters affecting ammonia degradation and energy consumption. To determine the presence of hydroxyl radicals, hydrogen peroxide was tested as an indicator because hydroxyl radicals are compounds that have a very short life when interacted to form  $\text{H}_2\text{O}_2$  (Gao *et al.*, 2001). Jin *et al.*

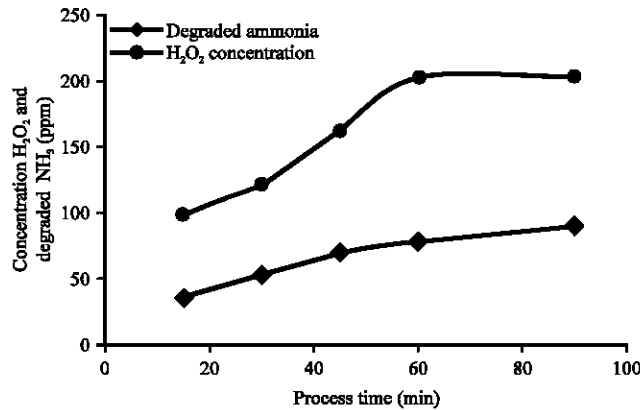


Fig. 2: Concentration profile of H<sub>2</sub>O<sub>2</sub> formed and ammonia degraded at 500 v and 60°C for 0.02 M KOH and 100 ppm ammonia

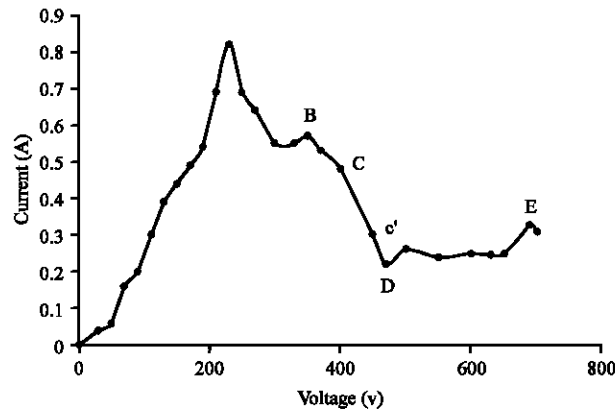


Fig. 3: Current profile vs. voltage in KOH solution during CGDE process

(2012) have reported that hydrogen peroxide production during the CDGE process can achieved concentration of 160 ppm. It shows that at the productive CGDE can produce hydrogen peroxide as a result of recombination of hydroxyl radicals.

The concentration of H<sub>2</sub>O<sub>2</sub> can be used to characterize the chemical active reactivity of hydroxyl radical in CGDE as it has long living chemical compound in the experiment (Jin *et al.*, 2012). Figure 2 illustrates the ratio of H<sub>2</sub>O<sub>2</sub> formed and degraded ammonia based on experimental results using KOH 0.02 M, ammonia concentration of 100 ppm, voltage 500 v and a temperature of 60°C. It can be seen from the Fig. 2 that the H<sub>2</sub>O<sub>2</sub> produced is higher than the degraded ammonia during the CGDE process with an average ratio of 2.45 to 1. This is due to the plasma electrolysis hydroxyl radicals are formed not only degrading the waste, but also recombines to form hydrogen peroxide (Liu *et al.*, 2010).

Figure 3 shows current product characteristic at variation of voltage applied during CGDE process. Jin *et al.* (2010) proposed 5 regions to explain the typical curve of Fig. 3, namely ohmic region ( $V < V_A$ ), limiting current region ( $V_A < V < V_B$ ), transition region ( $V_B < V < V_D$ ) and glow discharge electrolysis region ( $V > V_D$ ). In the ohmic region electrolysis of water took place and conventional electrolysis occurred with small bubbles of gas leaving the anode. In the limiting current region

bubbles were coalescing to the anode and the bubble coverage fraction increased.  $V_B$  was termed as the breakdown voltage in reference. In the transition region  $V_D$  was the critical voltage (also termed as midpoint voltage in reference). The transition region was also divided into three parts where sharp decrease was observed ( $V_B < V < V_C$ ), stabilized vapor sheath appeared around the anode ( $V_C < V < V_D$ ) and compact vapor sheath built up around the anode and progressively covered the anode surface ( $V_C < V < V_D$ ). Meanwhile, in the glow discharge electrolysis region the vapor sheath covered all active bubble nucleation sites of the anode; current transport happened through glow discharge (Jin *et al.*, 2010).

Figure 4 shows effects of anode depth on hydrogen peroxide, the chemical active reactivity of plasma (Jin *et al.*, 2012), produced during the CGDE process. The concentration of hydrogen peroxide increased with CGDE treatment time. The highest yield of hydrogen peroxide was obtained at a depth of anode 5 mm although the anode surface area more submerged than CDGE. Vapor sheath around the anode is sufficiently stable at higher surface area so that more vapors are produced when plasma is formed. Plasma shield formed are so large that they widen the collision zone between excited electrons and water vapor molecules and produce more hydroxyl radicals as well as hydrogen peroxide. Meanwhile, for CGDE with anode depth less than 5 cm produced less plasma shield and reduces the collisions between excited electrons and water vapor molecules and the amount of hydroxyl radicals as well as hydrogen peroxide formed are less. CGDE with anode depth of 10 mm will give more surface area but the effectiveness of the sheath around the anode is reduced so that all submerged anode are covered by water vapor. This reduces the collision zone between the excited electrons and water vapor and causes the electrons move to the anode conductively and the amount of hydroxyl radicals as well as hydrogen peroxide declined sharply.

Figure 4 shows the depth of the anode 5 mm and a 15 min process time is able to produce  $H_2O_2$  about 156 ppm (or 312 ppm OH radicals) by consuming energy of 201.6 kJ. The study reported by Jinzhang *et al.* (2008) with the same process time using a solution of  $Na_2SO_4$  and voltage of 600 v produced 22 ppm of OH radicals with energy consumption of 135 kJ. It indicated that the process of CGDE in this experiment has a high performance in generating OH radicals.

Figure 5 shows the effects of electrolyte concentration on degradation efficiency. It can be seen that at KOH 0.02 M has higher degradation efficiency than at 0.01. This is due to the more electrolyte ions produced that can conduct electrical current. The more the electrical current the more excited electrons to form plasma and the more ionized water vapor. This ionized water vapor

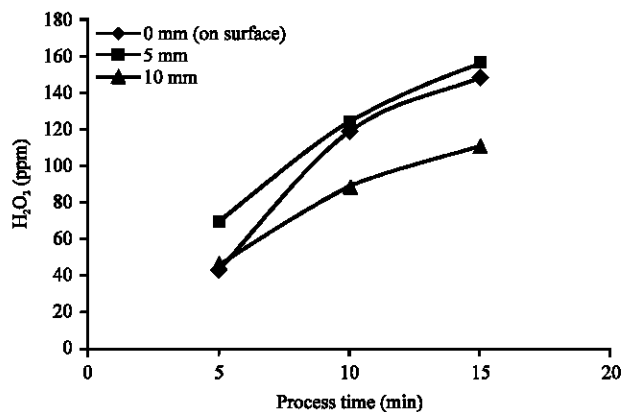


Fig. 4: Concentration profile of  $H_2O_2$  formed at several anode depths

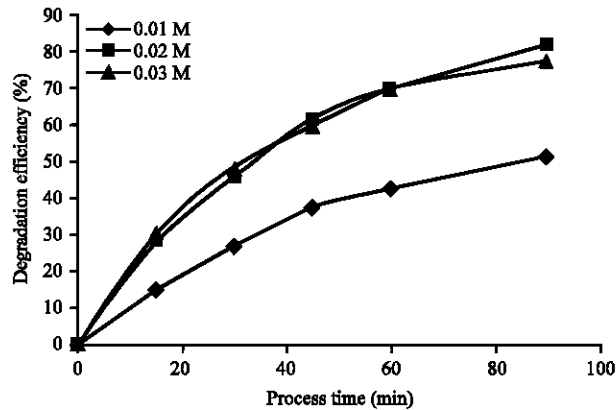


Fig. 5: Variation of ammonia degradation efficiency at several KOH concentrations at 700 v and 60°C for 0.02M KOH and 100 ppm ammonia

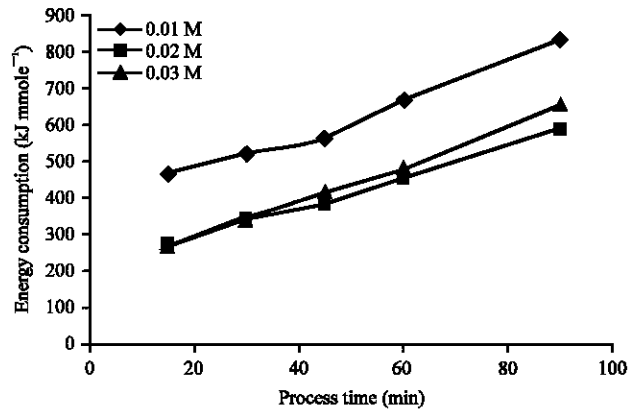


Fig. 6: Variation of energy consumption at several KOH concentrations at 700 v and 60°C for 100 ppm ammonia

will collide each other or diffuse to the solution and will strike the unionized water vapor to form hydroxyl radicals (Gao *et al.*, 2006). Therefore, there are more hydroxyl radicals are released to degrade ammonia at KOH 0.02 M than at 0.01 M. However, there is no significant different on degradation efficiency for KOH 0.02 and 0.03 M.

Figure 6 shows the effects of electrolyte concentration on energy consumption. Energy consumption for KOH 0.02 M is less than 0.01 M due to the ratio of hydroxyl radicals production as well as degradation efficiency for both concentrations are higher than the ratio of current needed for ammonia degradation. However, energy consumption for KOH 0.03 M is higher than 0.02 M as the current in the solution for KOH 0.03 M is higher than 0.02 M whilst the degradation efficiencies for both concentration are relatively equal. Therefore, energy needed to degrade a given amount of ammonia for KOH 0.02 M is less than for KOH 0.03 M.

The voltage also varied to see their effects on degradation efficiency as shown in Fig. 7. The voltage applied in the experiments are 500, 600 and 700 v, respectively, whilst the KOH and ammonia concentrations are 0.02 M and 100 ppm, respectively. Degradation efficiency increase 30.4% if the voltage is increased from 500 to 600 v. Meanwhile, degradation efficiency increase 16.4% if the voltage is increased from 600 to 700 v. At 500 v, plasma produced

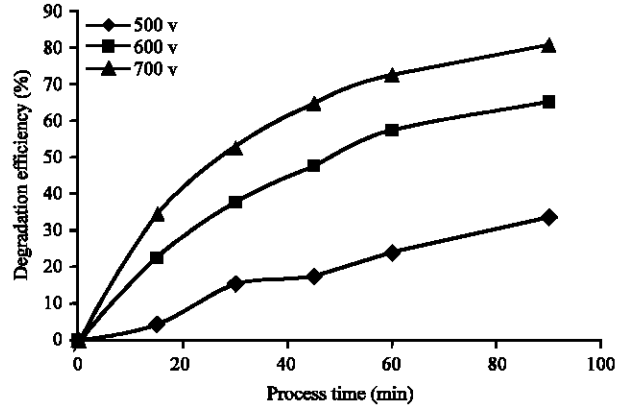


Fig. 7: Variation of ammonia degradation efficiency at several voltage applied in CGDE process

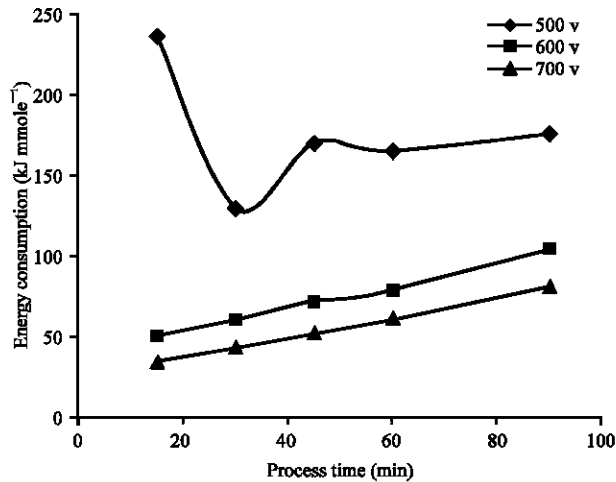


Fig. 8: Variation of energy consumption at several voltages applied in CGDE process

is least but produced the highest current as high as 0.376 A. The higher the current, the lower the resistances of sheath gas at the anode and the lower the production of ionized gas. The ionized gas has important role in breaking water molecule become hydroxyl radicals and hydrogen radicals so that the lower the ionized gas the lower the degradation efficiency. The optimum degradation efficiency achieved in the experiment was 89.2% at 700 v and 60°C using electrolyte KOH 0.02 M, while the energy consumption at such condition is 80 kJ mmole<sup>-1</sup>.

Figure 8 shows the effect of voltage applied on energy consumption in CGDE process. It can be seen that the higher the voltage the lower the energy consumption. The higher the voltage the higher the kinetic energy of electron that passes through its electrical fields. There are collisions among atoms and molecules during electron movement to anode causing energy transfer among atoms and produced heat. The higher the kinetic energy, the more the heat produced so that vapor formation in anode is higher due to Joule heating. Gas sheath around the anode will cut off the current to the anode so that excited electrons will dissociate water vapor to hydronium ion (H<sub>3</sub>O<sup>+</sup>) that can break water molecule to hydroxyl radicals, which have important role on ammonia degradation (Gao *et al.*, 2008). Energy needed to degrade ammonia at 500 v is as high as

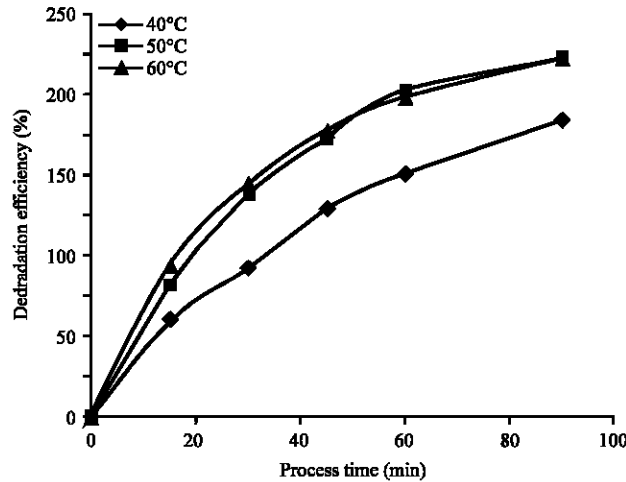
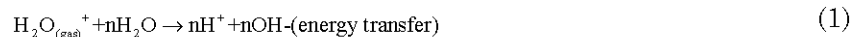


Fig. 9: Variation of ammonia degradation efficiency at several temperatures applied in CGDE process

175.7 kJ mmole<sup>-1</sup> due to the measured current is very high because of the resistance of sheath gas is lower than at 600 or 700 v. Meanwhile, at higher voltage the current tend to decrease as the resistance of sheath gas is increase. Therefore, the production of hydronium ion as well as ammonia degradation efficiency increases.

In the experiments, the temperature of SGDE process was maintained in the range of 30-60°C using cooling water. This is done to reduce the evaporation of ammonia due to the increasing rate of warming during CGDE process. Temperature of CGDE processes were varied 40, 50 and 60°C to observe the effect of temperature on the degradation of ammonia. Meanwhile, the voltage, KOH and ammonia concentrations are 700 v, 0.02 M and 100 ppm, respectively. Figure 9 shows the effects of temperature on ammonia degradation efficiency at such condition. Figure 9 shows that the lower the temperature the lower the ammonia degradation efficiency. This is due the lower the temperature, the more the heat absorbed by cooling water causing the lower the formation of sheath gas in anode which leads to the lower resistance. As a results, hydronium ion production (H<sub>3</sub>O<sup>+</sup>) was reduced and also the formation of hydroxyl and hydrogen radicals. Ammonia degradation efficiencies almost have the same values at operating temperatures of 50 and 60°C. This is due to the lower reaction constant at higher temperature so that it can interfere the concentration and the presence of hydroxyl radicals (Gao *et al.*, 2003). Plasma formed at higher temperature will produce higher sheath gas around the anode that lead the formation of hydroxyl radicals through ions hydronium mechanism and can increase the ammonia degradation efficiency.

Figure 10 shows the effect of temperature on energy consumption in the CGDE process. It can be seen that energy consumption at temperatures of 40°C is very high due to the lower resistance around the anode at other temperature so that increase the electrical current. On the other hand, hydroxyl radical production is decrease. Hydroxyl radical formation in CGDE occurs in two reaction mechanisms, namely charge transfer and energy transfer as indicated in the following reaction:





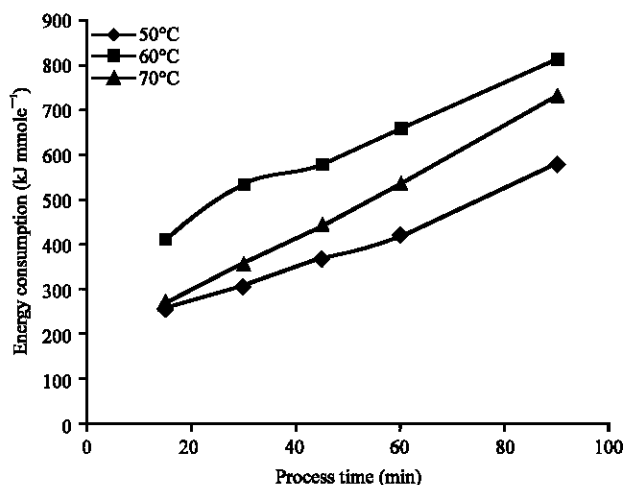
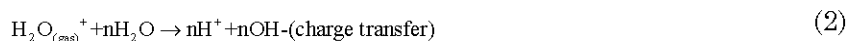


Fig. 10: Variation of energy consumption at several temperature applied in CGDE process



Charge transfer occurs in normal electrolysis process, while the energy transfer occurs in the plasma electrolytic process (Jin *et al.*, 2012). Based on the reaction mechanism described above, normal electrolysis phenomena dominate in the formation of hydronium ions that play an important role in generating OH radicals at range temperature of 30-40°C. Gao *et al.* (2003) found that for degradation reactions of red B and flavine G with CGDE, the rate constants decrease with the rise of temperature, which was different from that of normal reactions.

## CONCLUSION

Experiments have been conducted to degrade ammonia from wastewater through CGDE processes. The results show that the hydroxyl radicals produced is higher than the ammonia degraded during the CGDE process. In general, increasing potential discharge will increase electrical current. The highest yield of hydroxyl radicals was obtained at a depth of anode 5 mm although the anode surface area more submerged than CDGE. Ammonia degradation efficiency increase with increases in electrolyte concentration, voltage and temperature applied in the CGDE processes. The optimum condition is achieved using KOH 0.02 M at 700 v and 60°C, where at such condition ammonia degradation efficiency and energy consumption are 89.2% and 80 kJ mmole<sup>-1</sup>, respectively.

## ACKNOWLEDGMENT

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