Journal of
Environmental Science
and Technology

Research Article
Effect of Low Flow Rate of Air Injection on Remazol Red Degradation in Contact Glow Discharge Electrolysis Reactor

Tulus Sukreni, Setijo Bismo and Nelson Saksono

Department of Chemical Engineering, Faculty of Engineering, University of Indonesia, 16424 Depok, Indonesia

Abstract

Background and Objective: The plasma electrolysis requires a high amount of energy at the beginning of the process. The purpose of the study was to examine how air injection could reduce the energy of plasma formation. Furthermore, the effect of the flow rate of injected air on hydroxyl radical production and Remazol Red degradation were also studied. **Materials and Methods:** In this study, the air was injected directly through the glass sheath at the anode in Contact Glow Discharge Electrolysis reactor. Material used were Remazol Red RB-133 200 ppm as synthetic dye waste, Fe^{2+} 20 ppm as catalyst and Na_2SO_4 0.02 Mas electrolyte solution. **Results:** For the same energy input, the higher the flow rate of air injection, the radical hydroxyl concentration increased to an optimum point at a certain flow rate. Moreover, the rate of airflow at optimum condition increased with increasing voltage. An airflow rate of 0.05 L min^{-1} and a voltage of 600 V was the optimum condition. The concentration of hydroxyl radical at this condition produced 19.0849 mmol L^{-1} after 30 min. **Conclusion:** This was an increase of 48.43% in comparison with the amount of •OH where air injection was not used. The presence of air injection also increased the degradation of Remazol Red. Within 5 min, Remazol Red degradation had reached 86.37% at an airflow rate of 0.05 L min^{-1}. This indicated a 53.59% increase compared to the degradation process without air injection.

Key words: Air injection, contact glow discharge electrolysis, degradation process, optimal condition, Remazol Red

Corresponding Author: Nelson Saksono, Department of Chemical Engineering, Faculty of Engineering, University of Indonesia, 16424 Depok, Indonesia

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Azo dyes, such as Remazol Red, are the most widely used in the textile industry. The wide usage is due to its low price, stability and color variations. However, the industrial wastewater produced contains anionic dyes which makes it difficult to dispose of due to its complex aromatic structure and toxicity, not biodegradable[1].

The contact glow discharge electrolysis (CGDE) process is part of the Advanced Oxidation Process (AOP). It has been applied to several types of wastewater and has proven effective in reducing ammonia concentration[2], linear alkylbenzene sulfonate (LAS)[3] and degrading textile dye waste[1]. Previous research showed that the process degraded liquid waste which containing textile dyes such as Remazol Brilliant Blue by 96.15%[4], Brilliant Red B by 97.8%[5] and Acid Orange 7 by 95.33%[6] and 95.77%[7].

The CGDE process requires high energy at the beginning of the plasma formation[1,3-6]. The higher the energy consumed, the more stable the gas sheath around the anode and as a result, larger plasma is formed. The gas sheath and discharge formation are influenced by several process variables, such as the concentration and temperature of the solution and the position of the anode depth[8]. In addition, the air injection also reduces the energy of plasma formation and ease the discharge[9]. Optimization of the operating conditions improves the efficiency of energy used[2-6].

In contact glow discharge electrolysis, the energy produced during the process form highly reactive oxidants which may degrade the compounds in textile dye wastes. From several oxidants formed, hydroxyl radicals (·OH) are the very effective oxidants for the degradation process due to its large oxidation potential[10].

Previous research showed direct air injection affected the process of plasma formation. The higher the airflow rate, the dimmer the plasma formed[11,12]. The intensity of plasma formed during the CGDE process significantly influenced the production of ·OH. The dissociation process for the formation of ·OH decreased with smaller plasma. The high airflow rate in a previous experiment caused decrease in energy consumption during the process, lowered the amount of ·OH produced[4,11,12]. Therefore, the analysis of hydroxyl radical production was carried out with small air volume flow rate of 0.15, 0.05, 0.03 and 0.015 L min^{-1}.

MATERIALS AND METHODS

Study area: The research was conducted from October, 2017 to August, 2018 at the Process Intensification Laboratory of the Department of Chemical Engineering, University of Indonesia.
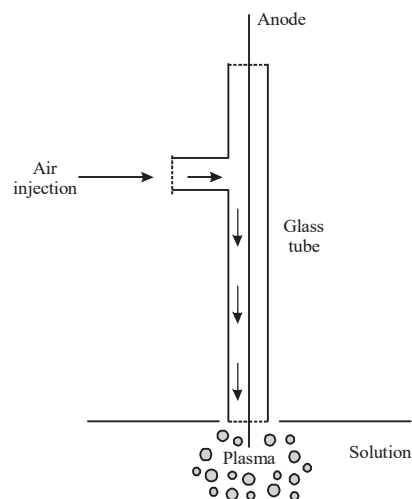

Fig. 1: Air injection on plasma
Source: Saksono *et al.*[12]

Research tools: The main tool used was the contact glow discharge electrolysis (CGDE) reactor[11]. In the reaction with the addition of gas, the air which was measured by flowmeter was injected using a compressor through the glass sheath on the 25 cm depth of anode as shown in Fig. 1.

Research procedure: Electrolyte solutions with concentration 0.02 M[13,14] were prepared by dissolving Na_2SO_4 in the distilled water. The dye waste used was synthetic Remazol Red RB-133 with an initial concentration of 200 ppm and Fe^{2+} 20 ppm as catalyst[15]. After materials and research tools preparation, some measurements were taken for ·OH production and calculation of energy consumption, followed by measurement of degradation of synthetic dye waste with variation of air volume flow rate of 0.15, 0.05, 0.03 and 0.015 L min^{-1}. The hydroxyl radical (·OH) formed during plasma electrolysis recombined to form H_2O_2. Therefore, the ·OH production was measured based on the concentration of H_2O_2 in Na_2SO_4 electrolyte solution using permanganometry titration. During the plasma electrolysis process, the energy consumption could be calculated as follows:

$$\text{Energy (watt)} = \text{Voltage (volt)} \times \text{Current (ampere)}$$

where, voltage values were regulated using a slide regulator and current values could be read using a multimeter. The measurement of degradation of Remazol Red RB-133 synthetic dye solution used UV-Vis Spectrophotometer BEL Photonics UV-M51. The analysis was carried out at a visible region with a strong absorbance of the azo group (chromophore) at 520 nm wavelength. The degradation calculation of Remazol Red dye concentration used the following Eq:

$$\text{Remazol red degradation} \left(\%\right) = \frac{C_o - C_t}{C_o} \times 110$$

where, C_0 is the initial concentration of Remazol Red and C_t is the concentration of Remazol Red at a certain time.

RESULTS

Figure 2a and b show the plasma was formed at a voltage of 700 V, 0.02 M Na_2SO_4, 55°C, the anode 25 mm depth with the condition without air injection and with air injection at a flow rate of 2 L min^{-1}, respectively. As shown in Fig 2b, the plasma formed at an airflow rate of less than 2 L min^{-1} is looked bigger and brighter. With a low airflow rate, the plasma formed was stable since the injected air does not interfere with the formation of the gas sheath around the anode.

The air injection positively affected the production of hydroxyl radicals as shown in Fig. 3. The longer the processing time, the more hydroxyl radicals produced in the air injection process. The increase in production of ˙OH at a certain time was relatively constant compared to the amount of ˙OH in conditions without air injection. The amount of air volume flow rate influenced the increase in ˙OH production. With the higher volume flow rate of air injection, the radical hydroxyl concentration increased to the optimum point. The optimum condition of the voltage of 600 volt in Fig. 3 was obtained at the air volume flow rate of 0.05 L min^{-1}. In 30 min CGDE
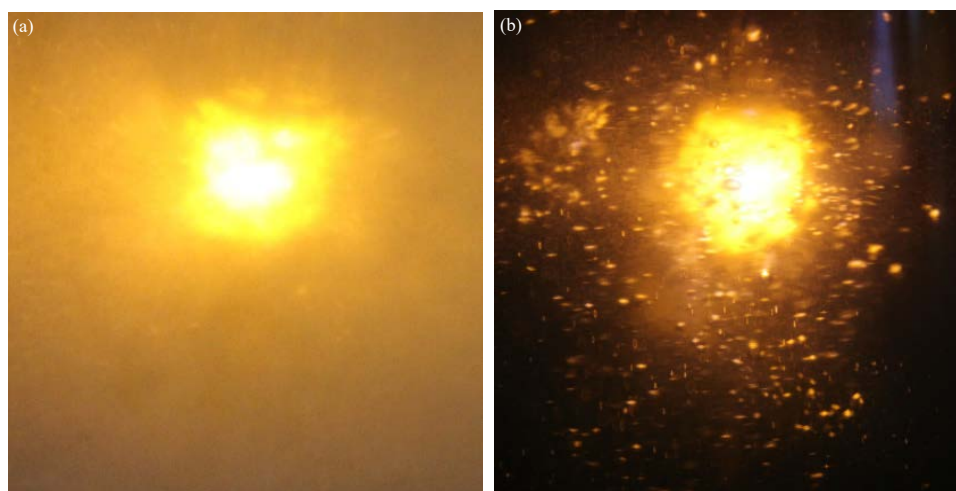

Fig. 2(a-b): Plasma was formed at a voltage of 700 V, 0.02 M Na_2SO_4, 55°C, the anode 25 mm depth with the condition, (a) Without air injection and (b) With air injection at a flow rate of 2 L min^{-1}
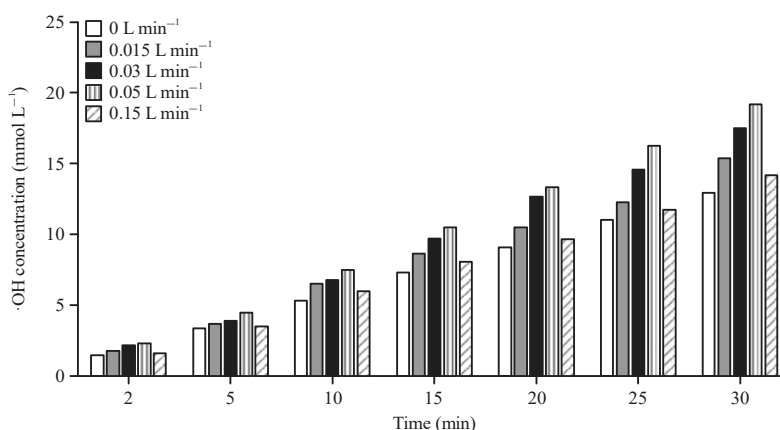

Fig. 3: Concentration of ˙OH formed at a voltage of 600 V, the concentration of electrolyte solution 0.02 M, anode depth of 25 mm, the temperature of a solution of 55°C with variable air volume flow rate
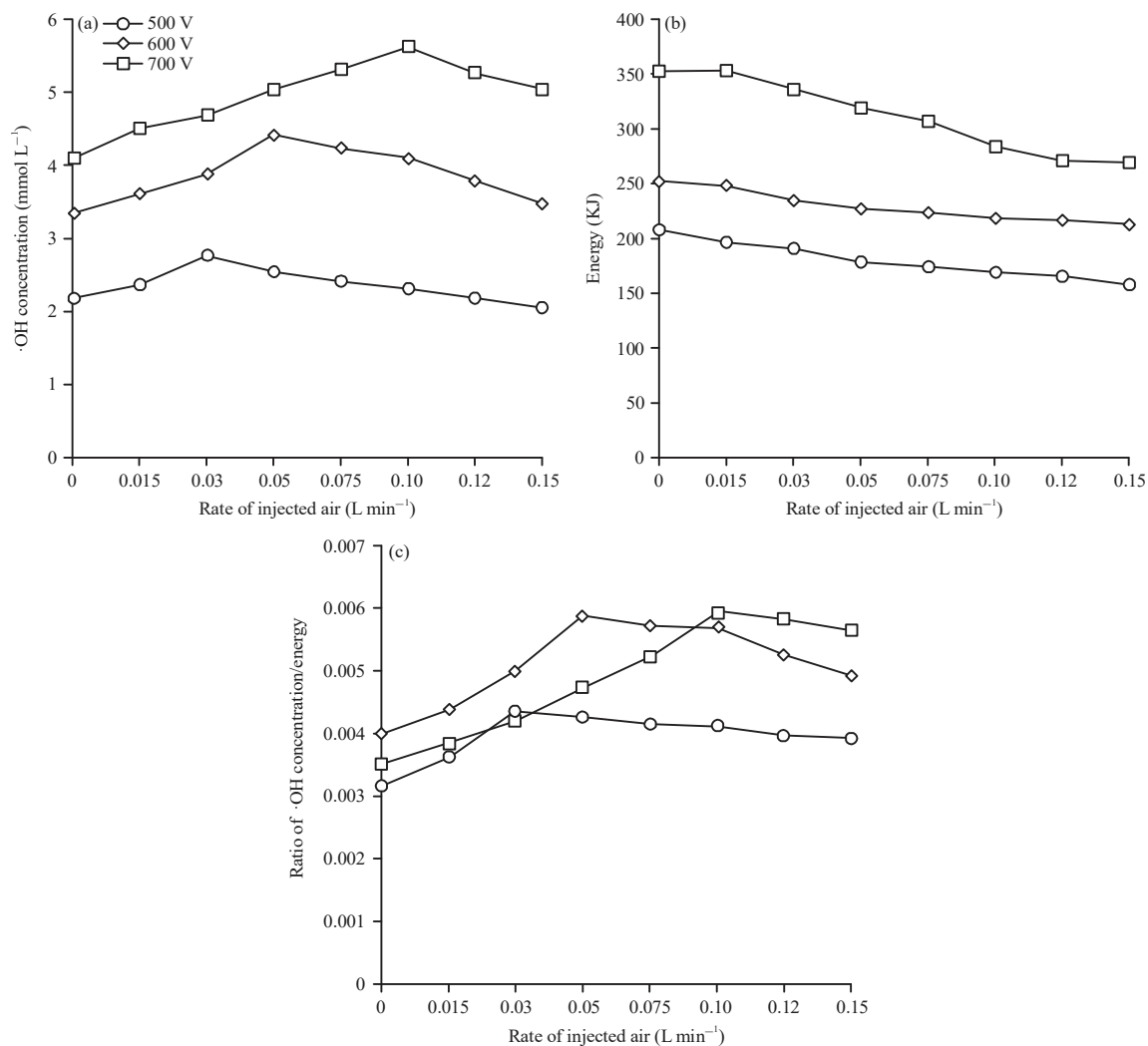
Fig. 4(a-c): Effect of air volume flow rate on, (a) Concentrations of ·OH, (b) Energy consumption with voltage variations on Na_2SO_4
0.02 M, anode depth of 25 mm and temperature of solution 55°C and (c) Ratio of production of concentration of ·OH
with energy consumption in voltage variations

process at the optimum conditions, the production of ·OH was 19.09 mmol L^{-1}, around 48.43% more than where air injection was used.

The increase of ·OH production and the optimum value was also influenced by the voltage used. The higher the voltage (energy), the greater the concentration of ·OH produced as shown in Fig. 4a. However, the presence of air injection reduces the amount of process energy as shown in Fig. 4b.

The ratio of the amount of production of ·OH to the energy needed during the contact glow discharge electrolysis process represents the efficiency as explained in Fig. 4c. For the condition without air injection, the highest process efficiency was obtained at a voltage of 600 V and the lowest at 500 V. Nevertheless, the efficiency at 500 V voltage increased

with air injection until it reached its optimum point at an airflow rate of 0.03 L min^{-1}. The rise efficiency was caused by the increased ·OH production as shown in Fig. 4a and the decrease of energy due to the increased airflow rate as shown in Fig. 4b. After reaching the optimum flow rate (0.03 L min^{-1}), the efficiency started declining. The air volume flow rate being greater than 0.03 L min^{-1} caused the plasma to be destabilized, leading to a decrease in ·OH production.

The process efficiency at 600 V was greater than at 500 V. At a higher voltage (energy), larger plasma formed and the greater ·OH produced. The increased ·OH production was in line with the increase in air volume flow rate injected until it reached its optimum conditions of 0.05 L min^{-1}. The process efficiency at 700 V was smaller than 600 V. A large amount of ·OH produced at voltage of 700 (Fig. 3a) did not improve the
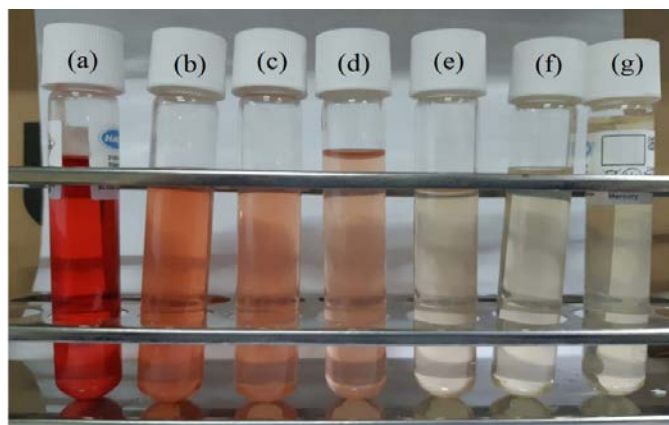
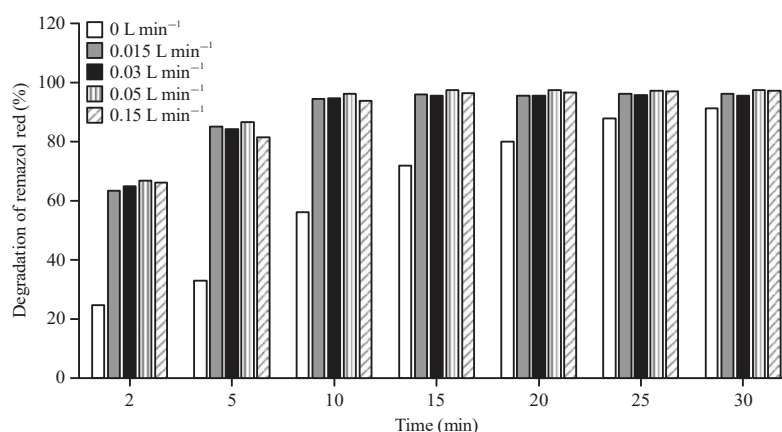Fig. 5(a-g): Degradation of Remazol Red at (a) 0, (b) 10, (c) 20, (d) 30, (e) 60, (f) 90 and (g) 120 min

Fig. 6: Degradation of dye waste at a voltage of 600 V, the concentration of 0.02 M electrolyte solution, anode depth of 25 mm, the temperature of a solution of 55°C with variable air volume flow rate for 30 min at 5 min intervals

Table 1: Concentration of ·OH, energy and process efficiency at an optimum airflow rate

Voltage (volt)	Optimum airflow rate (L min^{-1})	·OH concentration (mmol L^{-1})	Energy (watt)	Process efficiency [·OH]/energy
500	0.03	2.78	635	0.00437
600	0.05	4.44	756	0.00587
700	0.1	5.65	945	0.00597

efficiency because the energy needed to produce ·OH also increased (Fig. 3b). However, at 700 V, the efficiency continued to increase with air volume flow rate and reached an optimum point at the air volume flow rate of 0.1 L min^{-1} as shown in Table 1.

The CGDE process by air injection could be applicated in the textile dye waste treatment process. Remazol Red is included in the azo group with 2 nitrogen atoms (-N = N-) for chromophore[16]. Figure 5a-g show the degradation in color during the contact glow discharge electrolysis process at 0, 10,

20, 30, 60, 90 and 120 min, respectively. The red color at the beginning of the sample decreased and the solution looked clearer in 30 min.

From Fig. 6, the degradation process was faster in the beginning. However, after 15 min of contact glow discharge electrolysis process, the increase in degradation was insignificant. The Remazol Red degradation comparison to the production of ·OH with in 2 and 5 min were shown in Table 2. With the higher injection of airflow rate, the production of ·OH increased to the optimum point at an airflow rate of 0.05 L min^{-1}. Similarly, with the increase in the degradation of Remazol Red, higher airflow rate increased the degradation to the optimum point of a flow rate of 0.05 L min^{-1}. However, the increase in production of ·OH was not proportional to the degradation, where the amount of Remazol Red degraded was much larger than the amount of ·OH formed.

Table 2: Comparison between the increase in Remazol Red degradation and production of ˙OH for 2 and 5 min at a voltage of 600 V, the concentration of electrolyte solution 0.02 M, anode depth of 25 mm, solution temperature 55°C

Time (min)	Airflow rate (L min^{-1})				
	0	0.015	0.03	0.05	0.15
Degradation of Remazol Red					
2	24.67	63.34	64.87	66.54	66.25
5	32.77	84.73	84.00	86.37	81.51
Production of ˙OH					
2	1.434	1.747	2.150	2.285	1.568
5	3.360	3.629	3.898	4.435	3.494

Table 3: Value of COD, TOC and pH during the degradation process of Remazol Red at a voltage of 600 V, the concentration of electrolyte solution 0.02 M, anode depth of 25 mm, the temperature of solution 55°C

Time (sec)	Concentration (mg L^{-1})				pH
	Remazol red	COD	TOC	˙OH	
0	190.70	165.38	113.52	0.00	6
10	7.55	151.04	98.67	282.20	4
20	5.08	84.73	78.45	504.90	3
30	4.90	75.77	67.20	724.20	3
60	3.60	55.13	50.03	1255.45	3

The values of chemical oxygen demand (COD) and total organic carbon (TOC) obtained were listed in Table 3. In 30 min, the degradation process ran effectively. The Remazol Red concentration decreased significantly by 97.55% (from 190,7-4.9 mg L^{-1}) within 30 min and 98.95% (from 190.7-3.6 mg L^{-1}) in 60 min. The degradation process was followed by a reduction in COD values of 54.18% (from 165.38-75.77 mg L^{-1}) and 66.66% (from 165.38-55.13 mg L^{-1}) at 30 and 60 min, respectively. Furthermore, there was a decrease in TOC values of 35.09% (from 113.52-67.2 mg L^{-1}) at 30 min and 51.67% (from 113.52-50.03 mg L^{-1}) at 60 min. The decrease in COD and TOC indicated oxidation perfectly occurred, forming CO_2 and H_2O.
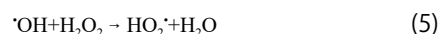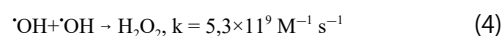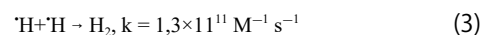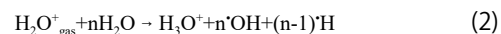
DISCUSSION

This research was successfully developed and increased plasma formation with lower flow rate of the air volume (<2 L min^{-1}) injected at the anode. With less energy condition, the CGDE process could increased the ˙OH production and Remazol Red degradation.

Water has a high dielectric constant ($\varepsilon r = 81$) and density ($\rho = 1100$ kg m^{-3}). Therefore, it required a large amount of energy to initiate discharge and plasma formation. Air injection reduces the energy of plasma formation and makes plasma discharges easier[9,17]. Additionally, the density of gas bubbles was smaller than water and therefore, the plasma formed by air injection looks bigger as shown in Fig. 2. This condition would affect the amount of ˙OH formed where the production of ˙OH by air injection was greater than the process without the air injection.

The process in the previous experiments used air injection with[11,12] a flow rate of more than 2 L min^{-1}. The gas sheath formed could be observed from the size of the plasma discharge[11], where the higher the flow rate of air injection, the smaller the plasma formed. With smaller energy consumption, the gas sheath formed was insufficiently stable and the discharge of plasma was smaller with dimmer light. The production of ˙OH decreases[9] with smaller plasma formation.

The amount of Remazol Red degraded was much larger than the ˙OH formed as describe in Table 2. This indicated the existence of other species[18] which reacted during the degradation process of Remazol Red. The radicals formed during contact glow discharge electrolysis processes, such as ˙O, ˙H and HO_2˙:

$$H_2O \rightarrow {}^{\bullet}O + H_2 \tag{1}$$

$$H_2O^+_{gas} + nH_2O \rightarrow H_3O^+ + n{}^{\bullet}OH + (n-1){}^{\bullet}H \tag{2}$$

$${}^{\bullet}H + {}^{\bullet}H \rightarrow H_2, \; k = 1,3 \times 11^{11} \; M^{-1} \; s^{-1} \tag{3}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2, \; k = 5,3 \times 11^9 \; M^{-1} \; s^{-1} \tag{4}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2{}^{\bullet} + H_2O \tag{5}$$

Other molecules formed, such as O_3, H_2O_2 and O_2, also acted as strong oxidizers with sequential oxidation potential values of 2.07, 1.78 and 1.23 V[7].

Injecting air containing oxygen and nitrogen increased the formation of ˙OH. Importantly, the dissociation of oxygen forms radicals which reacted with water to form ˙OH. This was based on the reaction in the gas phase as follows[19].

$$e + O_2 \rightarrow O^{\bullet} + O^{\bullet} + e \tag{6}$$

$$O^{\bullet} + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \tag{7}$$

Furthermore, the presence of nitrogen molecules dissociated water molecules to form ˙OH and ˙H[20] according to Eq. 8:

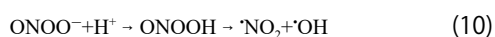$${}^{\bullet}N_2 + H_2O \rightarrow N_2 + {}^{\bullet}OH + {}^{\bullet}H \tag{8}$$
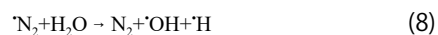
Additionally, the CGDE process connected to the surrounding air caused the formation of the reactive nitrogen species (RNS), such as peroxynitrite and NO_x. These species

also played a role in the degradation of organic dyes[18]. Peroxynitrite ($ONOO^-$) is a highly reactive species formed from the reaction of nitric oxide ($^{\bullet}NO$) and superoxide ($^{\bullet}O_2^-$) in the following Eq:

$$^{\bullet}NO + ^{\bullet}O_2^- \rightarrow ONOO^- \tag{9}$$

Peroxynitrite reactions with other molecules form peroxynitric acid (ONOOH) and the RNS compounds such as nitrogen dioxide ($^{\bullet}NO_2$) and dinitrogen trioxide (N_2O_3). Free radicals such as hydroxyl ($^{\bullet}OH$) are formed as shown in the following Eq:

$$ONOO^- + H^+ \rightarrow ONOOH \rightarrow ^{\bullet}NO_2 + ^{\bullet}OH \tag{10}$$

$$^{\bullet}NO + ^{\bullet}NO_2 \rightarrow N_2O_3 \tag{11}$$

The effectiveness of the degradation process by plasma electrolysis method was shown by the decrease in the value of chemical oxygen demand (COD) and total organic carbon (TOC) as shown in Table 3. Although the rate of degradation process after 10 min decreased, the plasma electrolysis process constantly produced $^{\bullet}OH$ and continued to oxidize the dissolved intermediate compounds. This could be seen from the COD value, which continued to decline. Moreover, the decreasing value of TOC along the process indicated the mineralization process was effective.

CONCLUSION

Less energy was needed for plasma formation with a higher flow rate of the air volume injected at the anode. The decrease of plasma formation energy was insignificant compared to the flow rate of air <2 L min^{-1}. Furthermore, the air injection increased $^{\bullet}OH$ production and Remazol Red degradation as an organic compound in textile dye waste.

SIGNIFICANCE STATEMENT

This study discover the usage of air injection during the contact glow discharge electrolysis (CGDE) process that can be beneficial for increasing the $^{\bullet}OH$ production and Remazol Red degradation. This study will help the researcher to uncover the critical areas of optimal flow rate of injected air that many researchers were not explore yet.

REFERENCES

1. Wang, X., M. Zhou and X. Jin, 2012. Application of glow discharge plasma for wastewater treatment. Electrochimica Acta, 83: 501-512.
2. Saksono, N., B.P. Adiwidodo, E.F. Karamah and S. Kartohardjono, 2013. Contact glow discharge electrolysis system for treatment of wastewater containing ammonia. J. Environ. Sci. Technol., 6: 41-49.
3. Saksono, N., T. Sukreni and N. Zulfakhri, 2016. Degradation of linear alkylbenzene sulfonate using multi-anode contact glow discharge electrolysis. J. Environ. Sci. Technol., 9: 329-334.
4. Averous, F., D.M. Zairin and N. Saksono, 2018. Remazol brilliant blue degradation using contact glow discharge electrolysis reactor with air injection and NaCl solution. E3S Web Conf., Vol. 67. 10.1051/e3sconf/20186704043.
5. Yan, Z., Y. Liu, W. Ren and Z. Yuan, 2012. Investigation of liquid plasma catalysis on Ti electrodes for the decolorization of a brilliant red B solution. J. Electrostat, 70: 48-53.
6. Jin, X., H. Bai, F. Wang, X. Wang, X. Wang and H. Ren, 2011. Plasma degradation of acid Orange 7 with contact glow discharge electrolysis. IEEE Trans. Plasma Sci., 39: 1099-1103.
7. Jin, X., H. Zhang, X. Wang and M. Zhou, 2012. An improved multi-anode contact glow discharge electrolysis reactor for dye discoloration. Electrochimica Acta, 59: 474-478.
8. Saksono, N., D.A. Putri and D.R. Suminar, 2017. Degradation of Remazol Red in batik dye waste water by contact glow discharge electrolysis method using NaOH and NaCl electrolytes. AIP Conf. Proc., Vol. 1823. 10.1063/1.4978077.
9. Ruma, M.A. Habib, S.H.R. Hosseini, T. Sakugawa and H. Akiyama, 2015. Treatment of wastewater by underwater discharge in gas bubbling water. Int. J. Renewable Energy Environ. Eng., 3: 189-194.
10. Yang, Y., Y.I. Cho and A. Fridman, 2012. Plasma Discharge in Liquid: Water Treatment and Applications. CRC Press, Boca Raton, Florida.
11. Sukreni, T., N. Saksono and S. Bismo, 2018. Air injection effect on energy consumption and production of hydroxyl radicals at plasma anode. J. Environ. Sci. Technol., 11: 132-138.

12. Saksono, N., T. Sukreni, A.L. Naibaho and S. Bismo, 2018. Effect of direct air injection through anode in plasma electrolysis process for batik dye wastewater treatment. E3S Web Conf., Vol. 67. 10.1051/e3sconf/20186701008.

13. Sukreni, T., N. Saksono and S. Bismo, 2018. Effect of anode depth and conductivity of electrolyte solution on energy consumption in plasma electrolysis. IOP Conf. Ser. Earth Environ. Sci., Vol. 105. 10.1088/1755-1315/105/1/012009.

14. Saksono, N., I. Puspita and T. Sukreni, 2017. Application of contact glow discharge electrolysis method for degradation of batik dye waste Remazol Red by the addition of Fe^{2+} ion. AIP Conf. Proc., Vol. 1823, No. 1. 10.1063/1.4978076.

15. Sukreni, T., N.S. Amelinda, N. Saksono and S. Bismo, 2018. Optimization of Fe^{2+} addition for degradation process of textile dye waste using contact glow discharge electrolysis with air injection. E3S Web Conf., Vol. 67. 10.1051/e3sconf/20186703031.

16. Shen, Y.J., L.C. Lei and X.W. Zhang, 2008. Evaluation of energy transfer and utilization efficiency of azo dye removal by different pulsed electrical discharge modes. Chin. Sci. Bull., 53: 1824-1834.

17. Ahmed, M.W., R. Suresh, J.K. Yang, S. Choi and H.J. Lee, 2016. Effect of water conductivity on the generation of OH• radicals in high frequency underwater capillary discharge. Int. J. Renew. Energy Environ. Eng., 4: 28-34.

18. Jamroz, P., A. Dzimitrowicz and P. Pohl, 2018. Decolorization of organic dyes solution by atmospheric pressure glow discharge system working in a liquid flow through mode. Plasma Proces. Polym., Vol. 15, No. 1. 10.1002/ppap.201700083.

19. Yasuoka, K. and K. Sato, 2009. Development of repetitive pulsed plasmas in gas bubbles for water treatment. Int. J. Plasma Environ. Sci. Technol., 3: 22-27.

20. Magureanu, M., D. Piroi, F. Gherendi, N.B. Mandache and V. Parvulescu, 2008. Decomposition of methylene blue in water by corona discharges. Plasma Chem. Plasma Process., 28: 677-688.