

Degradation of Remazol Brilliant Blue Using Plasma Electrolysis Method with NaCl and Fe²⁺ Ion Addition

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Abstract. Remazol Brilliant Blue is a dye waste mostly generated by the textile industry and can be very dangerous to the environment. Plasma electrolysis is a method that can produce hydroxyl radicals in large quantities in order to degrade the dye compounds. This study aims to test the ability of plasma electrolysis method to degrade Remazol Brilliant Blue wastewater using NaCl as electrolyte, with the addition of Fe²⁺ ion and air injection. Before the degradation process was carried out, permanganometric test was performed to see the production of hydroxyl radicals with the variations of electrolyte concentration and voltage. The degradation process were investigated more specifically by looking at the effect of Fe²⁺ ion concentration and the initial concentration of Remazol Brilliant Blue. Remazol Brilliant Blue degradation reached 98.5% in 30 minutes where the initial concentration of Remazol Brilliant Blue is 100 ppm, voltage of 750 V, NaCl concentration 0.03 M, with the addition of 40 ppm Fe²⁺ ion and air injection. The results show that plasma electrolysis with NaCl as electrolyte using air injection has a good potential in degrading dye wastewater in the environment.

1 Introduction

The textile industry is one of Indonesia's most rapidly – growing and prospective industries. The industry employs a huge number of people and contributes to the nation's income. However, the industry comes with several negative impacts. One of the most visible impact is the environmental pollution from liquid dye waste, which is discharged without being treated by SME (Small and Medium Enterprise). Dye waste is one of the heavy organic compounds which are difficult to degrade naturally by the microorganism. Therefore, research on methods to effectively and appropriately process dye wastewater for SMEs need to be done.

Plasma electrolysis method is a proven method that can degrade liquid waste compounds from the textile industry in terms of the percentage of degradation and processing time. Plasma electrolysis method produces reactive species of H₂O₂, •OH, H•, and e⁻ [1]. These reactive species are produced due to the high potential difference of the electrodes. The degradation of textile waste can occur due to the presence of hydroxyl radicals and other reactive species that act as oxidizing agents in degrading waste.

The effectiveness of the plasma electrolysis method depends on the reactivity of the ion, electron, and radical species within the solution. Therefore, addition of

electrolytes in certain amount of concentration are required to increase the solution's conductivity. However, in order for the technology to be appropriately used by the SMEs in the textile industry, a relatively cheap and easily obtainable electrolyte is needed. A potential electrolyte that can be used is NaCl, which can be obtained from table salt.

However, due to the extreme reactivity of hydroxyl radicals, the compounds can create bonds between hydroxyl radicals to form H₂O₂, which has a lower oxidizing ability than hydroxyl radicals [2]. Therefore, addition of Fe²⁺ ions to prevent recombination of hydroxyl radicals to H₂O₂ through the Fenton reaction [1] is required. In this research, air injection is done in the plasma electrolysis process to reduce energy consumption.

The dye waste model used in this research is Remazol Brilliant Blue, commonly found and widely used in the Indonesian textile industry. Remazol Brilliant Blue has a molecular formula C₂₂H₁₆N₂Na₂O₁₁S₃ with a molecular weight of 626.53 g/mol. This research aims to evaluate the degraded liquid dye waste using the plasma electrolysis method and analyse the effects of voltage, NaCl concentration, addition of Fe²⁺, and initial concentration of waste on the degradation of Remazol Brilliant Blue.

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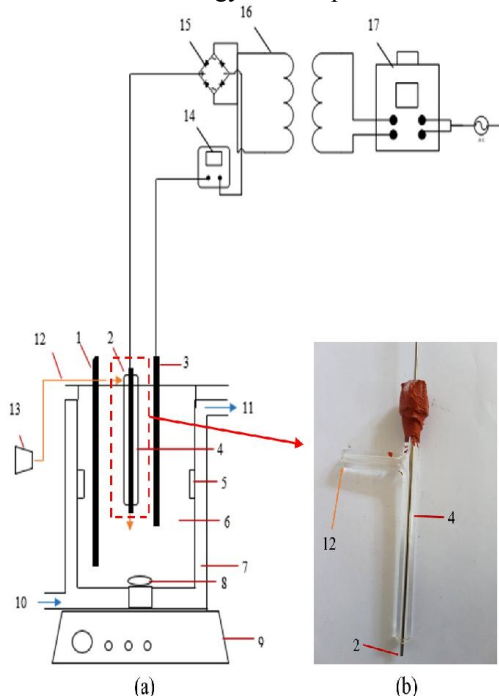
2 Experimental Section

2.1 Materials

This research used Remazol Brilliant Blue as waste, NaCl as the electrolyte solution, and Fe₂SO₄·7H₂O as addition ions. The production of hydroxyl radicals were tested with the permanganometric titration using KMnO₄, H₂SO₄, dan Na₂C₂O₄.

2.2 Instrumentation

The main equipment in this research is a Plasma Electrolysis Reactor as seen in the instrument diagram in Figure 1. The electrical circuit consists of a transformer, a slide regulator, and a diode bridge. The reactor is equipped with an external cooled circulating system to control the temperature. A tungsten anode and a stainless-steel cathode is used. The anode is coated with quartz glass to keep the contact area constant and for air injection to reduce energy consumption.



- | | |
|-------------------------|--------------------------|
| 1. Thermometer | 10. Cooling Water Input |
| 2. Anode | 11. Cooling Water Output |
| 3. Cathode | 12. Air Injection Input |
| 4. Quartz Glass | 13. Compressor |
| 5. Baffle | 14. Multimeter |
| 6. Waste Solution | 15. Diode Bridge |
| 7. Cool Water Container | 16. Transformer |
| 8. Magnetic bar | 17. Slide Regulator |
| 9. Magnetic stirrer | |

Fig. 1. Configuration of Plasma Electrolysis Instrumentation (a) Circulator Reactor Configuration, (b) Anode that Partially Coated by Quartz Glass

2.3 Procedure

The research begins with the current and voltage characterization to determine where the plasma will

form. The NaCl concentration was varied at 0.02 M; 0.03 M; and 0.04 M.

Measurement of hydroxyl radicals were analysed using a variety of process voltage and NaCl electrolyte concentrations. Measuring of the hydroxyl radicals formed only use an electrolyte solution to avoid mixing with the batik dye waste *Remazol Brilliant Blue*. The hydroxyl radicals are identified by measuring H₂O₂ concentrations with the permanganometric titration method.

Next, the degradation of Remazol Brilliant Blue was done for 30 minutes and analysed with a UV-Vis spectrophotometer with a variation of initial waste concentrations and Fe²⁺ concentrations. The amount of degradation was calculated with the following equation (equation 1):

$$\text{Percentage of degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \% \quad (1)$$

C₀ = Initial concentration (ppm)

C_t = Final concentration (ppm)

3 Results and Discussion

3.1 Characterization of the Voltage-Current

Figure 2 shows that a higher electrolyte concentration relates to a higher current. This is due to the higher number of ions in the solution becoming conductors of electricity. As the conductivity of the solution increases, it will makes the electrons to flow easier.

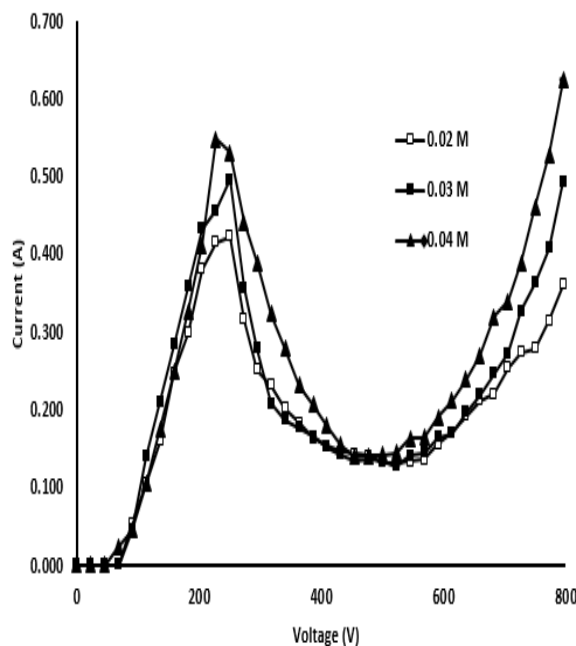


Fig. 2. Characterization of Volage-Current with Variation of NaCl Concentration

The higher the electric current, the easier it was for gas bubbles to form in the anode, decreasing the voltage needed to form plasma [3]. Thus, the higher the

electrolyte concentration, the higher the I_B and the lower the V_B needed as shown in Table 1.

Table 1. V_B dan I_B in current – voltage characterization at various NaCl concentrations

NaCl Concentration	V_B (Volt)	I_B (A)
0.02 M	250	0.42
0.03 M	250	0.49
0.04 M	227	0.55

3.2 Effect of NaCl Concentration in Hydroxyl Radical Production

Hydroxyl radicals are compounds that have low retention time, making it difficult to measure in solutions. Therefore, H_2O_2 , which are recombinant compounds of hydroxyl radicals, were used to indicate the presence of hydroxyl radicals. Radical hydroxyl production tests were carried out with permanganometric titration.

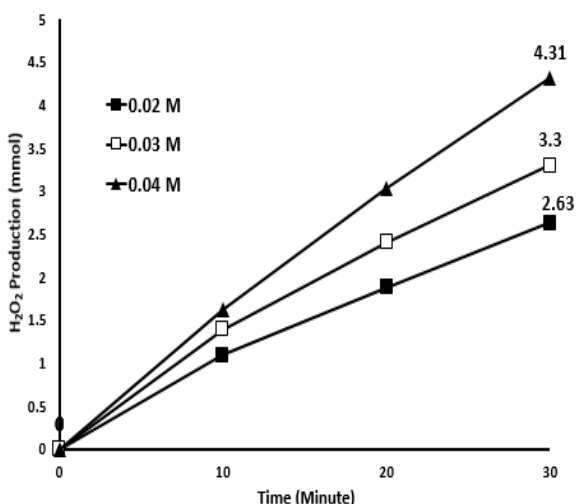


Fig. 3. Effect of Electrolyte Concentration to H_2O_2 Production with 750 V

Figure 3 shows that hydroxyl radicals production was highest at NaCl concentration of 0.04 M. This is because conductivity is directly proportional with the concentration of electrolytes as the high number of ions become conductors.

With the increase of ions as the carriers of electrons, the possibility of electrons being excited become higher and plasma tends to form more quickly. This caused hydroxyl radicals to form more quickly [4]. Increase in conductivity caused an increase in current density and power dissipation around the anode, causing easier formation of plasma and gas sheath [5].

Figure 4 shows that at the same concentration of NaCl, radical hydroxyl production increased with an increase in operational voltage. This is because the formation of active species become faster with a higher operational voltage [6].

When the voltage increased, kinetic energy from the electrons passing through a magnetic field increases and creates heat. The heat accelerates the formation of gas sheath during the plasma electrolysis process. This caused water vapour to be excited and breaks down the water molecules, forming hydroxyl radicals.

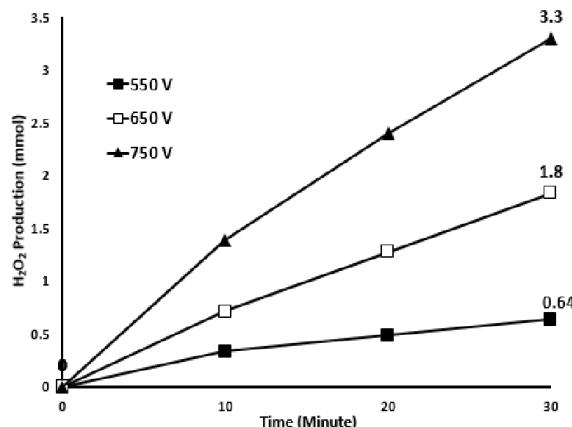


Fig. 4. Effect of Voltage to H_2O_2 Production with NaCl Concentration 0.03 M

3.3 Effect of Fe^{2+} Addition in Degradation of Remazol Brilliant Blue

The effect of adding Fe^{2+} on the degradation of Remazol Brilliant Blue is shown in Table 2. At the initial Remazol Brilliant Blue concentration of 100 ppm, the increase of Fe^{2+} addition increased the degradation of *Remazol Brilliant Blue*. At the 30th minute, the degradation of *Remazol Brilliant Blue* reached its highest point at 98.5% with the addition of 40 ppm of Fe^{2+} . Meanwhile, degradation of the dye waste without addition of Fe^{2+} only reached 71.93%.

Table 2. Effect of Ion Fe^{2+} Addition on the Degradation of Remazol Brilliant Blue 100 ppm, NaCl 0.03 M, Voltage of 750 V

Time (Minute)	Degradation (%)		
	0 mg/L Fe^{2+}	20 mg/L Fe^{2+}	40 mg/L Fe^{2+}
0	0	0	0
3	9.46	42.19	69.94
6	22.18	48.87	86.70
8	25.69	61.63	91.23
10	27.36	61.94	93.75
15	45.36	80.55	95.96
20	55.82	86.82	97.46
25	61.30	90.45	97.88
30	71.93	92.85	98.50

It can be observed that degradation without addition of Fe^{2+} was not effective. This is caused by the unoptimized contact time between hydroxyl radicals and *Remazol Brilliant Blue*. Hydroxyl radicals, which are not stable, easily recombine with other hydroxyl radicals to

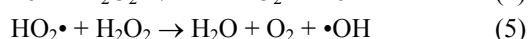
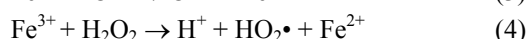
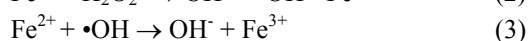
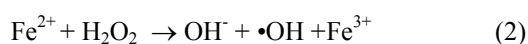
form H₂O₂ which can decrease the degradation effectiveness. The potential oxidation value of radical hydroxyl is 2.8 mV compared to 1.78 mV for H₂O₂ [7]. Addition of Fe²⁺ was done to increase the effectiveness of the degradation process. The Fe²⁺ added to the plasma electrolysis process came from FeSO₄. Addition of Fe²⁺ to the system increased the effectiveness of the process because Fe²⁺ can breakdown H₂O₂ and form hydroxyl radicals through the Fenton reaction [1]. This is evidenced by the results shown in Table 2 where a 20 and 40 ppm addition of Fe²⁺ significantly increased the degradation value.

A similar trend is shown on the degradation of Remazol Brilliant Blue with initial concentration of 150 ppm. From Table 3 it can be observed that without addition of Fe²⁺, the degradation process of Remazol Brilliant Blue was not effective, only reaching 55.26%. Meanwhile, the degradation process of *Remazol Brilliant Blue* with addition of 40 and 60 ppm of Fe²⁺ increased significantly, reaching 96.15% and 98.31%, respectively.

Table 3. Effect of Ion Fe²⁺ Addition on the Degradation of Remazol Brilliant Blue 150 ppm, NaCl 0.03 M, Voltage of 750 V

Time (Minute)	Degradation (%)			
	0 mg/L Fe ²⁺	20 mg/L Fe ²⁺	40 mg/L Fe ²⁺	60 mg/L Fe ²⁺
0	0	0	0	0
3	5.61	25.57	41.91	51.95
6	13.53	39.37	67.27	71.36
8	20.69	44.61	73.55	82.62
10	25.12	44.68	82.88	88.83
15	31.97	58.74	88.35	94.16
20	41.19	67.19	93.41	96.07
25	52.25	74.73	95.02	96.56
30	55.26	76.66	96.15	98.31

The degradation rate of the dye generally increased with an increase in the addition of Fe²⁺. The reaction between Fe²⁺ and H₂O₂ creates hydroxyl radicals which are stronger oxidizers than H₂O₂. The formation reaction of hydroxyl radicals are shown in equations 2-5 [8].



Besides hydroxyl radicals, the reaction between Fe²⁺ and H₂O₂ resulted in the formation of Fe³⁺ ions which can react and form Fe²⁺ [6]. This means that the higher number of Fe²⁺ in the solution will cause more H₂O₂ to turn into hydroxyl radicals. In turn, a higher number of hydroxyl radicals will increase the degradation rate of the dye in the liquid waste, increasing the effectivity.

However, the similar trend is not shown in Table 4 where it can be observed that addition of Fe²⁺ does not

have significant effects on the degradation of 250 ppm Remazol Brilliant Blue. This is caused by the high initial waste concentration and addition of Fe²⁺ becomes insignificant as hydroxyl radicals can directly react with waste without recombining into H₂O₂. Hydroxyl radicals are powerful oxidators in degrading organic waste, but have low selectivity. This causes hydroxyl radicals to rapidly degrade waste in high concentrations of waste.

Table 4. Effect of Ion Fe²⁺ Addition on the Degradation of Remazol Brilliant Blue 250 ppm, NaCl 0.03 M, Voltage of 750 V

Time (Minute)	Degradation (%)		
	40 mg/L Fe ²⁺	60 mg/L Fe ²⁺	80 mg/L Fe ²⁺
0	0	0	0
3	48.63	32.34	46.39
6	60.13	51.34	55.97
8	67.35	62.86	65.37
10	72.10	68.47	74.14
15	79.04	80.49	86.72
20	87.61	86.06	90.30
25	90.44	88.03	92.58
30	93.80	95.11	94.61

3.4 Effect of Initial Dye Waste Concentration on the Degradation of Remazol Brilliant Blue

Table 5 shows the degradation value of *Remazol Brilliant Blue* at different levels of initial concentration while adding the same concentration of Fe²⁺. From the table it can be observed that a higher initial concentration of dye waste will result in a smaller degradation of *Remazol Brilliant Blue*.

Table 5. Effect of Initial Dye Waste Concentration on the Degradation of Remazol Brilliant Blue, NaCl 0.03 M, Voltage of 750 V, and Addition of Fe²⁺ Ion 40 ppm

Time (Minute)	Degradation (%)		
	100 ppm RBB	150 ppm RBB	250 ppm RBB
0	0	0	0
3	69.94	41.91	48.63
6	86.7	67.27	60.13
8	91.23	73.55	67.35
10	93.75	82.88	72.1
15	95.96	88.35	79.04
20	97.46	93.41	87.61
25	97.88	95.02	90.44
30	98.5	96.15	93.8

This is because for a higher concentration of dye waste, more addition of Fe^{2+} is needed. Insufficient addition of Fe^{2+} will cause the rate of degradation to decrease as the number of catalysts are insufficient for the same number of oxidants. [9].

When the number of decomposed H_2O_2 that form hydroxyl radicals are not maximal, the time required to degrade the dye waste increases. Besides that, the decrease in degradation is due to the formation of intermediate products during the plasma electrolysis process. The higher initial dye waste concentration, the competition between initial reactants and intermediate products to react with active species will increase. This causes a decrease in the degradation percentage with a higher initial concentration. [10].

4 Conclusion

This research has successfully shown that the plasma electrolysis method is capable of degrading Remazol Brilliant Blue with a NaCl solution and air injection. An increase in the initial dye waste concentration requires an increase in the addition of Fe^{2+} . The maximum degradation reaches 98.5% at an initial dye waste concentration of 100 ppm with addition of Fe^{2+} 40 ppm and voltage of 750 V.

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