Optimization of Fe^{2+} addition for degradation process of textile dye waste using contact glow discharge electrolysis with air injection

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Abstract. This research determined the optimum concentration of Fe^{2+} to degrade waste textile dye by Contact Glow Discharge Electrolysis (CGDE) method with air injection. The addition of Fe^{2+} ions can increase the degradation rate of the dye waste due to the radical catalytic conversion of H_2O_2 producing OH radicals that play a significant role in the degradation process. Remazol Red was used as a dye synthetic dye which was degraded using a batch reactor equipped with continuous cooling water. Experimental results showed that waste concentrations of 100, 200, 300 and 400 ppm obtained the optimum Fe^{2+} concentration at 10, 20, 30 and 40 ppm, respectively. The higher concentration of dye waste indicated the higher the Fe^{2+} ion requirement to decrease the textile dye waste.

1 Introduction

The textile industry is one of the significant contributors to national income and employment sector in Indonesia. Based on the National Industrial Development Master Plan (RIPIN) in 2015-2035, the development of the industrial sector becomes a priority to contribute significantly to the national economic growth [1]. However, environmental pollution problems begin to occur since the majority of the home textile industry dispose waste into rivers without any further processing. Wastewater treatment problems, such as the absence of waste treatment installations or not using adequate technology to treat such waste, can cause damage to the environment around the textile plant.

Contact Glow Discharge Electrolysis (CGDE), or so-called plasma electrolysis is one of the proven research technologies that can be used for liquid wastewater degradation. Plasma electrolysis uses OH radicals as an active agent that can degrade waste more effectively and efficiently regarding time and rate of degradation [2]. Plasma in CDGE is formed due to the presence of a high potential difference between two electrodes, where it produces highly reactive compounds such as OH radicals and H radicals. Highly reactive OH radicals can form bonds between OH radicals producing H_2O_2, which has oxidation ability below the OH radicals. Metal ion Fe^{2+} can increase the rate of degradation in organic compounds since it reacts with H_2O_2 to produce OH radicals [3]. However, the addition of Fe^{2+} ions is not only directly proportional to the ability of waste degradation, but also there is a point where the addition of Fe^{2+} ions will make OH convert back into H_2O_2. Therefore, the addition of Fe^{2+} ion will be optimal under a certain condition. Meanwhile, the addition of air injection in the degradation process of CGDE method has proven to increase the effectiveness of the process in degrading textile dye waste of Remazol Red RB 133. The effectiveness of the process can be seen from the increase of OH radical production and degradation percentage, the decrease in process energy consumption and also the decrease of COD and TSS [4]. Unfortunately, the air dispersed within the reactor causes contact and the reaction that occurs has not occurred optimally. This research will be carried out with the addition of air is injected directly in the anode as well as the addition of metal ions Fe^{2+} during waste degradation process to improve the effectiveness of the process.

2 Materials and Method

The main tool used in this research is the CGDE reactor where the scheme is illustrated in Figure 1. The reactor used is a batch system, which is completed with the jacket as circulating cooling water. The cathode used is a cylindrical cathode with a diameter of 6 mm and an anode with a diameter of 0.5 mm wrapped in a glass tube. The voltage source for the reactor was directly obtained from the State Electricity Company (PLN), which maintained by using slide regulator, transformer, and a diode bridge. The multimeter was used to measure the flow of CGDE process. This research used the Na_2SO_4 solution as an electrolyte and varying the Fe^{2+} concentration of 0 ppm, 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm, and 60 ppm and variation of initial waste concentration of 100 ppm, 200 ppm, 300 ppm, and 40 ppm. The test was carried out for 30 minutes with a

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temperature of 55°C. Sampling for the degradation test was performed at minutes 0, 3, 6, 8, 10, 15, 20, 25, and 30.

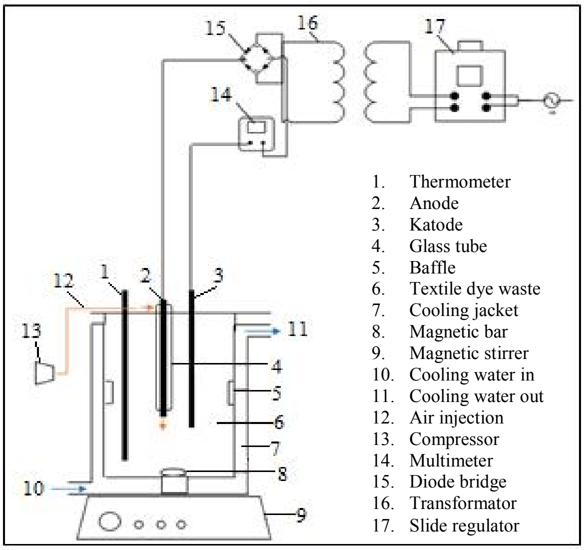

Fig 1. The circuit schematic of plasma electrolysis reactor

3 Results and Discussion

3.1 The Optimum Concentration of Fe^{2+}

The results of the research on the textile dye waste degradation process of Remazol Red by using CGDE method and air injection by varying the initial concentration of waste and the concentration of Fe^{2+} addition can be seen in Figure 2.

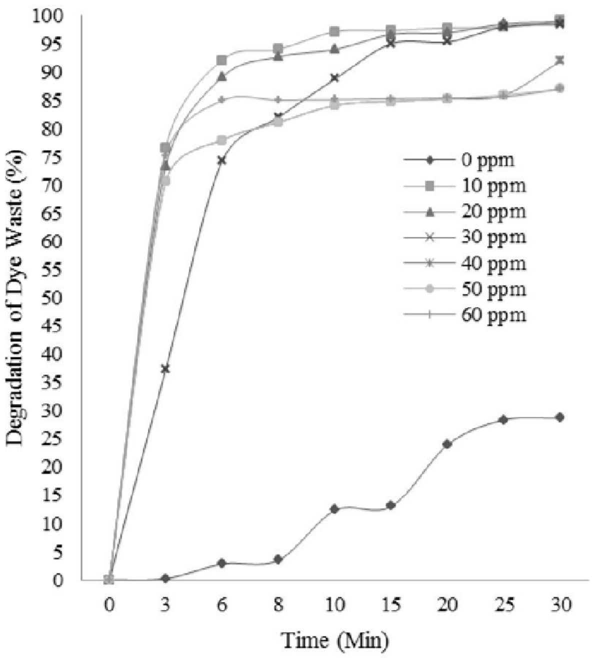

Fig. 2. The catalytic effect of Fe^{2+} on 100 ppm of dye waste

Figure 2 shows the longer the degradation process, the more degraded dye waste. The best degradation result was shown at the Fe^{2+} concentration of 10 ppm with the degradation percentage of 99.04% (Table 1). When the concentration of Fe^{2+} was increased, the percentage decreased from 20 ppm to 60 ppm. Also, the smallest degradation percentage was in the absence of Fe^{2+} addition of 28.76%.

Table 1. The catalytic effect of Fe^{2+}on 100 ppm of dye waste

Concentration of Fe^{2+}	Time (min)	Concentration of RR (ppm)	Degradation rate (%)
0 ppm	0	85.2	28.76
	30	60.7	
10 ppm	0	89.4	99.04
	30	0.86	
20 ppm	0	103.6	98.93
	30	1.11	
30 ppm	0	96.3	98.50
	30	1.44	
40 ppm	0	113.3	92.07
	30	8.99	
50 ppm	0	113.3	87.10
	30	14.62	
60 ppm	0	103	87.07
	30	13.32	

In contrast to the results of waste with an initial concentration of 100 ppm, waste with a concentration of 200 ppm requires more $FeSO_4$ to reach the optimum.

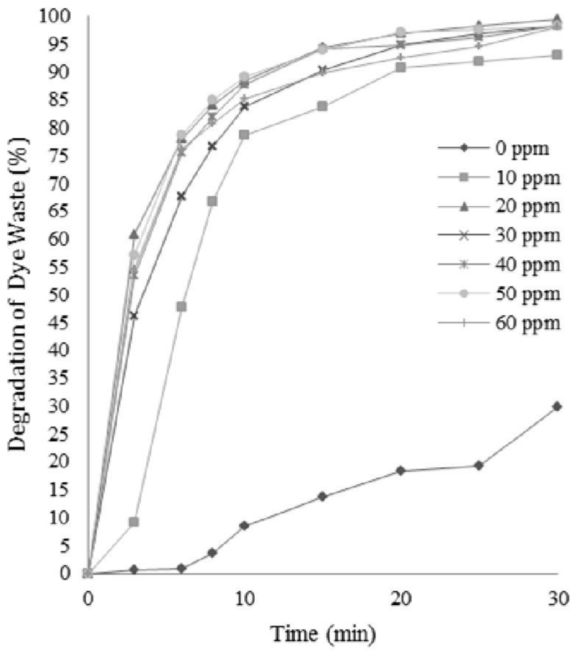

Fig. 3. The catalytic effect of Fe^{2+} on 200 ppm of dye waste

Figure 3 shows the highest degradation results at a Fe^{2+} concentration of 20 ppm with degradation percentage of 99.35%. The smallest degradation percentage was in the absence of Fe^{2+} addition of

28.76%. When the concentration of Fe^{2+} is increased, the percentage decreased from 30 ppm to 60 ppm (Table 2).

Table 2. The catalytic effect of Fe^{2+} on 200 ppm of dye waste

Concentration of Fe^{2+}	Time (min)	Concentration of RR (ppm)	Degradation rate (%)
0 ppm	0 30	182.5 128.1	29.81
10 ppm	0 30	157.7 11.28	92.85
20 ppm	0 30	212 1.38	99.35
30 ppm	0 30	186.2 3.14	98.31
40 ppm	0 30	215.5 3.8	98.24
50 ppm	0 30	197.5 3.51	98.22
60 ppm	0 30	184.6 3.57	98.07

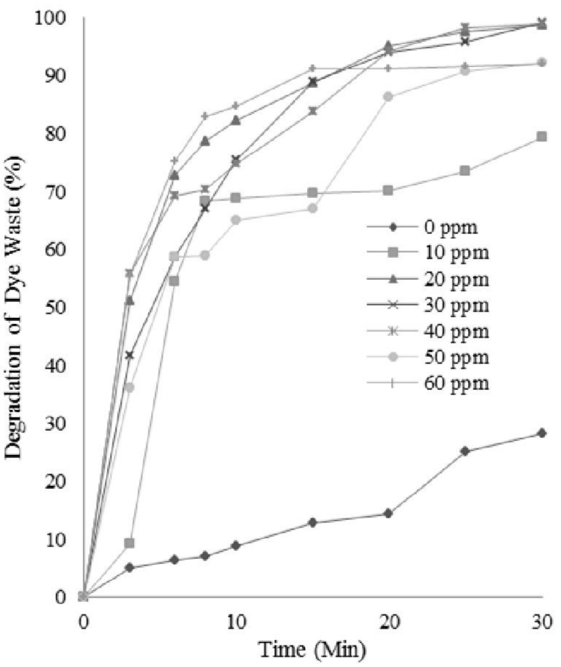

Fig. 4. The catalytic effect of Fe^{2+} on 300 ppm of dye waste

For a waste concentration of 300 ppm, the degradation process performed without the addition of Fe^{2+} showed a very small degradation percentage of 28.19% as shown in figure 4. Moreover, when the addition of Fe^{2+} was 10 ppm, 20 ppm and 30 ppm the degradation percentage increased. However, in the addition of Fe^{2+} at 40 ppm to 60 ppm, the percentage of waste degradation tends to decreased as can be seen in Table 3.

Table 3. The catalytic effect of Fe^{2+} on 300 ppm of dye waste

Concentration of Fe^{2+}	Time (min)	Concentration of RR (ppm)	Degradation rate (%)
0 ppm	0 30	293.7 210.9	28.19
10 ppm	0 30	255.7 52.8	79.35
20 ppm	0 30	372.3 4.69	98.74
30 ppm	0 30	266.7 2.48	99.07
40 ppm	0 30	308.6 3.48	98.87
50 ppm	0 30	303.2 23.67	92.19
60 ppm	0 30	352 27.63	92.15

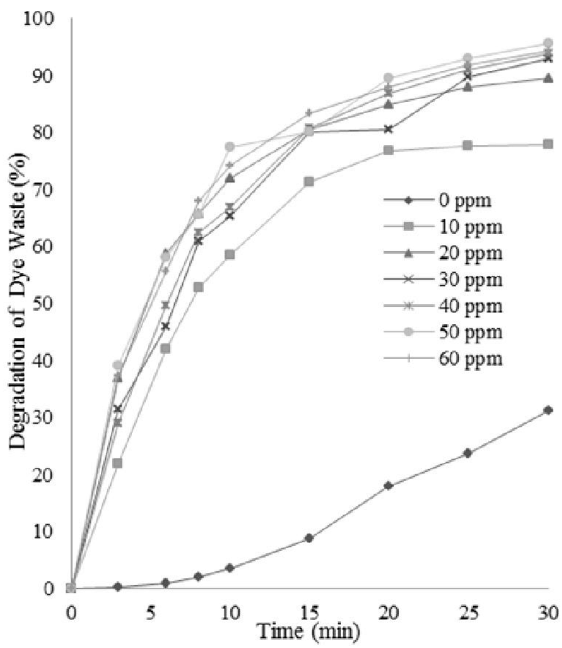

Fig. 5. The catalytic effect of Fe^{2+} on 400 ppm of dye waste

The highest degradation percentage for the initial waste concentration of 400 ppm was 95.77% with the addition of Fe^{2+} concentration of 50 ppm. Along with the increase in Fe^{2+} addition concentration, there is also increase of degradation percentage up to 50 ppm, but when the concentration reached 60 ppm, the degradation percentage decreased up to 94.27% (Table 4). From the data above, the optimum values of Fe^{2+} addition on each initial concentration of Remazol Red dye waste are as follows (Table 5). In Table 5, it is seen that the optimum Fe^{2+} values for each waste yield different degradation percentage. It can be seen that the waste with 400 ppm concentration has the smallest degradation percentage of 95.7%. This is related to the thirty-minute process time where the higher concentration of waste, the longer the time to degrade.

Table 4. The catalytic effect of Fe^{2+} on 400 ppm of dye waste

Concentration of Fe^{2+}	Time (min)	Concentration of RR (ppm)	Degradation rate (%)
0 ppm	0 30	350.3 241.3	31.12
10 ppm	0 30	341.7 75.5	77.90
20 ppm	0 30	344.75 35.98	89.56
30 ppm	0 30	362.1 25.04	93.08
40 ppm	0 30	410.25 25.25	93.85
50 ppm	0 30	372.2 15.76	95.77
60 ppm	0 30	353.3 20.25	94.27

Table 5. Concentration of Dye Waste with Concentration Fe^{2+}

Concentration of Dye Waste	Fe^{2+} Concentration	Degradation Rate
100 ppm	10 ppm	99.08%
200 ppm	20 ppm	99.35%
300 ppm	30 ppm	99.07%
400 ppm	40 ppm	95.77%

The absence of Fe^{2+} compounds in the dye waste degradation process is still considered ineffective where OH radicals contact with textile dye waste was still not optimal. OH radicals that have a short residence time of 3.7 x 10^{-9} s makes the OH radicals to have unstable properties and will readily recombine with other OH radicals forming H_2O_2 which can reduce the effectiveness of the process. Ion Fe^{2+} can convert H_2O_2 into OH radical based on the Fenton reaction [3,5].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad k_1 = 76\ M^{-1}s^{-1} \tag{1}$$

In addition to generating OH radicals, the reaction between Fe^{2+} and H_2O_2 can also produce Fe^{3+} ions, which can react to form Fe^{2+} [6]. Thus, it can be concluded that the more Fe^{2+} in the solution, the more H_2O_2 can be converted back into OH radicals which are useful for accelerating the degradation rate of textile dye waste to a certain point and improving the process efficiency. However, the addition of Fe^{2+} ions has an optimum limit that if the addition of Fe^{2+} has crossed the limit, it will reduce the effectiveness of the process so the degradation process will decrease [7].

$$Fe^{2+} + {\bullet}OH \rightarrow Fe^{3+} + OH^- \quad k_2 = 4{,}3 \times 10^8 M^{-1}s^{-1} \tag{2}$$

The reaction equation above shows that the excessive addition of Fe^{2+} can also consume OH radicals by considering the value of k_2 is greater than the value of k_1. So the need to Fe^{2+} addition to each waste was different due to the needs of OH radicals.

Figure 6. Sample 200 ppm, 20 ppm Fe^{2+}

The color change showed the possibility of reaction occurred due to the addition of $FeSO_4$ substances with oxidizing compounds in the reactor, especially O_2 (Figure 6). $FeSO_4$ was oxidized to form a yellowish compound, which is the by-product of ferric oxide and ferric sulfate. The more $FeSO_4$ were added to the process, the more compounds were oxidized therefore the yellowish color will appear more concentrated. The oxidation reaction occurred is as follows

$$12FeSO_4 + 3O_2 \rightarrow 4Fe_2(SO_4)_3 + 2Fe_2O_3 \tag{3}$$

$$12FeSO_4.H_2O + 3O_2 \rightarrow 12Fe(OH)SO_4 + 6H_2O \tag{4}$$

3.2 Effect of Air Injection and Energy Consumption

The addition of air injection to the dye waste degradation process, the energy consumption resulting from this process becomes lower (Table 6). The addition of air injection in the CGDE process could facilitate the formation of plasma because the dielectric strength of the gas is lower than the solution. At a lower voltage, the plasma is already formed and the energy requirement becomes smaller [10]. Energy can be calculated by the following formula:

$$W = V \cdot I \cdot t \tag{5}$$

Also, the oxygen present in the air can also increase the production of OH radicals [8] according to the reaction as follows:

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

$$O^{\bullet} + H_2O \longrightarrow OH^{\bullet} + OH^{\bullet} \quad (7)$$

$$OH^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} + O^{\bullet} \quad (8)$$

The formation of O radicals which has a sufficiently high oxidation number increases the effectiveness of waste degradation where the oxidation value of OH, O, O_3 and H_2O_2 radicals respectively is 2.8; 2.42; 2.07; and 1.78 [9].

Table 6. Energy Consumption

Dye Waste Concentration	Fe^{2+} Concentration	I (A)	Energy Consumption (kJ)	Energy Consumption (kJ/mmol)
100 ppm	10 ppm	0.298	184.833	413.779
200 ppm	20 ppm	0.361	231.158	474.886
300 ppm	30 ppm	0.424	279.924	829.519
400 ppm	50 ppm	0.324	206.532	629.700

4 Conclusion

This study described the addition of Fe^{2+} effect on degradation process of textile dye by CGDE method. The greater the initial concentration of waste, the greater the concentration of Fe^{2+} added. Remazol Red dye waste with 100 ppm concentration reached optimal condition when degraded using the Fe^{2+} ion addition of 10 ppm with 99.08% degradation percentage. For waste with an initial concentration of 200 ppm was Fe^{2+} ion of 20 ppm was used with degradation percentage of 99.35%. For 300-ppm wastes, the optimum process will be obtained with the addition of 30 ppm Fe^{2+} ions to have degradation percentage of 99.07%. For waste with an initial concentration of 400 ppm, the optimal condition when Fe^{2+} ions of 50 ppm were added. The result of this process was 95.77% degradation. The addition of air injections can improve the degradation process of textile dyes, and also decrease energy consumption during the degradation process.

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