Comparison of the effectiveness electrocoagulation of dye (batik waste water) using iron and zinc as an anodes

S. Suhartana*, P. Purwanto*, Adi Darmawan**

*Doctoral Program in Environmental Science Diponegoro University
*Post Graduate Diponegoro University
**Inorganic Chemistry Laboratory, Chemistry Departement, Faculty of Sciences and Mathematics, Diponegoro University

Corresponding author: suhartana@live.undip.ac.id

Abstract This study aims to obtain dye (batik waste water) treatment by electrocoagulation with optimal results. The performance of electrocoagulation process was carried out in batch reactor. Four variables were taken which thought to greatly influence the electrocoagulation process, such as: distance between electrodes, voltage, acidity (pH) and electrolysis time. In this process, samples of 20 mL were taken out from the batch at 5, 10, 15, 20, 25, 30, 35, 40, 45 dan 50 minutes of contact time. Results obtained show that the most effective removal efficiency could be achieved at alkaline condition. Research that has been done shows that the percentage of wastewater treatment results is strongly influenced by the four variable changes. The study demonstrated that the lowest degradation efficiency occours at acid pH, while an increase temperature has only a slight effect on the electrocoagulation process. The maximum results from the electrocoagulation processes was obtained, with determine by measurement of chemical oxygen demand (COD). The results showed that, iron is better used as an anode than zinc. The effectiveness electrocoagulation reached optimal at 96.54% (at Fe anode) and 81.65% (at Zn anode), at alkaline condition (pH > 9), electrolysis time of 30 minutes, electrode distance of 1 cm and temperature at 70°C.

Keywords: electrocoagulation, variables of process, effectiveness electrocoagulation

1. Introduction

Based on the 2015 CIA World Factbook data, more than 7.2 billion people life on the earth. Human needs food, clothing and residence. Human growth is very rapid, but the earth as planet living is permanent. Growing trend in global population, urbanization and industrialization towards achieving high quality of life and well-being of the population has resulted high amount of gas, waste water and solid wastes being generated. It is very natural for the earth to become increasingly dense, healthy of living needs are also become increasing difficult, residence increasing difficult, clothing and environmental problems. The garment factory has wastewater treatment standards as determined by the Government of the Republic of Indonesia such as PP No: 32 Tahun 2009 concerning Environmental Protection and Management and PP No.82 / 2001 concerning water quality management and water pollution control. But in contrast, to medium and small clothing factories, they were easily dispose of the dye into the environment. If this problems uncontrolled, the health of the
environment and the comfort of human life must be disrupted, the earth would be an excess of carrying capacity. Research on batik/ textile industrial wastewater treatment has been carried out and reported. There are several methods such as electrocoagulation methods, electrode-composition, electrodecolorization and electrosorption methods. Research on textile wastewater treatment has done. For example, a review of research that examined the problem of batik /textile wastewater treatment [1]. The other studies confirmed that the processing of carbon felt (CF) dye waste as an electrode in the electrochemical process using Fenton reagent had good results [2]. There is also a report state that the electrocoagulation process was able to reduce the quantity of toxic (arsenic) material in wastewater [3], and the use of an electrochemical process combined with a chemical process, could be used to treat sugar mill waste [4]. Amazingly, about 84% of COD is able to be reduced, and about 88% of the color of sugar factory waste can be removed. The factory has also been carried out by Galvanic, Galvanic Fenton, and Hydrogen peroxide systems as reported by Delgado, et al (2018) [5]. With the galvanic method (using Fe as an electrode), at a pH of 2.8 and H2O2 / Fe3+ a ratio of 19: 1 (ie 7840 mg H2O2 / L and 408 mg Fe3+/L) can reduce COD 71%, eliminate color by 76%, total Organic carbon is 79% and the degradation process is up to 43%. The previous studies reported a satisfying results of the degradation process of Reactive Black 5 with Electrochemical Oxidation using a stable anode and stainless steel cathode as electrode material, with NaCl as a supporting electrolyte [6].

In the last 15 years, some researchers reported the success of the electrocoagulation method. Chen, (2004) was reported electrocoagulation (EC) is an electrochemical waste water treatment technology which has been used in treating effluents containing suspended solids, oil and grease, and even organic and inorganic pollutants that can be flocculated [7]. This method is characterized by simple equipment and easy operation. The next study emphasized, EC having a short reaction retention period and have no chemical additive and a lesser amount of precipitate or sludges at processing [8]. Usually, in EC processes, aluminum or iron plates are used as an electrode. Canizрасов et al, (2007) was reported that aluminum electrodes are the best option with regard to the adsorption of cationic reagent species (aluminum hydroxide) on the surface [9]. The further study emphasize it by using aluminum as a sacrificial electrode, EC processes have been successfully used in removal of COD as high as 56% from landfill leachate [10], improved into 86% from reactive dye bath effluent [11] and more improvement reported until 90% from oil suspensions [12].

The process of "dyeing" or coloring and the process of "wedel" or dyeing batik cause a high source of water pollution, it is necessary to do waste treatment. There are 3 types of liquid waste treatment technology, namely biologically, chemically, physics and even a combination of three methods. The method that is often used to treat batik industry wastewater is a combination of the three. This is as done by Rahmawati, et al (2009) who processed batik waste by electrocoagulation method, with good results (82%) [13]. The other study, processed batik wastewater by electrocoagulation method using Fe electrodes which shows a very good results (92%) [14]. This was confirmed by a similar studies, using indigo karmina dyes with around 95% decolorization [15].

The above studies, most of them still use mono / uni-variables. This means that the percentage of success of the pollutant material decomposition process is only measured by one variable. So the data presented is a graph that illustrates the percentage of the efficiency of electrocoagulation versus contact time, efficiency of electrocoagulation versus pH, the efficiency of electrocoagulation versus electrode distance and the efficiency of electrocoagulation versus temperature. The results showed that the electrocoagulationaon results reached optimal at 96.54% (at Fe anode) and 81.65% (at Zn anode), electrode distance of 1 cm, at alkaline condition (> from pH 10), electrolysis time of 30 minutes and temperature at 70°C.

2. Experimental
2.1 Material
Standart dye of Batik (Remazol black T purity > 98%), HCl and NaOH. Metal Iron and Zinc metal as electrodes (anodes). Carbon as cathode.
2.2 Experimental procedure
In this study, the experiments were carried out in batch reactor consisting of a 600 mL glass beaker and were equipped with single cathode and anode. The electrodes used are made of iron (as anode) and carbon (as cathode) installed parallel with the dimensions of 1 mm X 60 mm X 150 mm. The total effective electrode area was 90.0 cm² and the distance between electrodes was various at 0.5-3.5 cm. In each run, approximately 500 mL of total volume of dye (batik waste water) sample were placed in the beaker. The electrodes were then connected to a direct current from DC power supply (0-30V, 3.0A) with ammeter and voltmeter in the circuit. The magnetic stirrer was also used in this experiment to ensure a good mixing where the mixing rate was set constant at 100 rpm. The same procedure was done for zinc (as anode) and carbon (as a cathode). The experimental setup is presented in Figure 1.

![Figure 1. Schematic diagram of electrocoagulation experimental equipment](image)

2.3 Experimental procedure
In this experiment, the batch reactors were run at 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 minutes with pH range 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14. All the experiments were performed at a constant room temperature (26°C). At the end of each reactor, the solution with flocks was allowed to settle for 30 minutes in the beaker before chemical analysis. Then, after filtered, was taken at the limpid phase and analysed immediately using FAS or ferrous ammonium sulfate [Fe(NH₄)₂SO₄] according to Titrimetric Method. The changes of pH value in solution during the electrocoagulation processes was measured by a pH meter model Orion 5 star, while the temperature and conductivity were measured by a conductivity meter model YSI 30.

4. Results and Discussion
Based on the results of research conducted in the laboratory, there are several factors that can affect the percentage of the results of the electrocoagulation process, namely: 1. Distance between the cathode and anode, 2. Time of electrocoagulation 3. Degree of acidity of the electrocoagulation system, and 4. Types of electrodes (anodes) used. The electro-coagulation method is a reduction and oxidation (redox) reaction that occurs during the dyeing process. Reduction occupy in dyes, oxidation reaction was occurred in anodes (iron or zinc metal).

4.1 Effect of Electrodes (Anodes)
From the research data obtained the percentage of the results of the electrocoagulation process using iron metal as a cathode is 94.45%. While the percentage of the results of the electrocoagulation process using zinc metal was 82.34%. Actually the two metals (Fe and Zn) are equally capable of being good anodes, because both metals have a positive cell potential price, meaning both metals are easily oxidized, because the oxidation potential of Iron is 0.44 volts and oxidation potential 0.74 volt zinc [16]. The percentage of the results of the electrocoagulation process using iron metal electrodes is slightly better (94.45%), when compared with the percentage of the results of the electro-coagulation
process using Zinc metal (82.34%) this is thought to be due to the difference in the price of yield times the solubility of the two hydroxide salts. \( K_{sp} \text{Fe(OH)}_3 \) is 3.1 \( \times \) 10\(^{-36} \) while \( K_{sp} \text{Zn(OH)}_2 \) is 3.1 \( \times \) 10\(^{-17} \), it seems very striking differences. This will have an impact on the ease of formation of hydroxide deposits. The price of \( K_{sp} \text{Fe(OH)}_3 \) is smaller so that the hydroxide salt tends to settle more easily, and then forms a floc which is useful for adsorbing the dye / dye in the waste water.

4.2 Electrocoagulation in an acidic atmosphere

The electrocoagulation process is strongly influenced by the acidic atmosphere. Because metal (both Fe and metal Zn) will usually dissolve easily in an acidic atmosphere. The presence of metal cations (Fe\(^{3+} \) and Zn\(^{2+} \)) greatly determines the amount of solubility results from the hydroxide salts (Fe(OH)\(_3\) and Zn(OH)\(_2\)). Easily the correlation between the percentage of electrocoagulation and the acidic solution atmosphere can be seen in Figure 2.

![The relationship Percentage of electrocoagulation and pH in an acidic atmosphere](image)

**Figure 2.** Relationship between the percentages of electrocoagulation with pH in an acidic conditions

4.3 Electrocoagulation in a Basa Atmosphere

The electrocoagulation process is strongly influenced by the atmosphere. Because the metal (both Fe and Zn metal) after dissolving in an acidic atmosphere, then the cation (both Fe\(^{3+} \) and Zn\(^{2+} \)) in an alkaline atmosphere will form its hydroxide salts (Fe(OH)\(_3\) and Zn(OH)\(_2\)). If the multiplication of \([\text{Fe}^{3+}]\) and \([\text{OH}^-]\) exceeds the price of the results of the solubility of Fe(OH)\(_3\), a precipitate of Fe(OH)\(_3\) will occur. Likewise if \([\text{Zn}^{2+}]\) and \([\text{OH}^-]\)^2 exceed the price of the result of the solubility of Zn(OH)\(_2\) there will be Zn(OH)\(_2\) deposition. However, at a certain pH, it does not change the concentration of hydroxide ions, so that the resulting deposits also remain. This results in a fixed yield of hydroxide (Fe(OH)\(_3\) and Zn(OH)\(_2\)). Easily the correlation between the percentage of electrocoagulation and the atmosphere of the base solution can be seen in Figure 3.
4.4 Effect of Time on Electrocoagulation percentage

The electrocoagulation process is strongly influenced by the time of the reaction contact. This is in line with Faraday's law to \( W = \frac{e \cdot i \cdot t}{9500} \). Where \( W \) is the weight of the electrocoagulation deposit, \( e \) is the molecular weight of the material which is reduced, \( i \) is the current strength and \( t \) is the time needed in the electrocoagulation process. However, at a certain time it appears that the results of the electrocoagulation results are constant, this is due to the equilibrium process between the electrocoagulation process (\( \text{Fe(OH)}_3 \) and \( \text{Zn(OH)}_2 \)). More optimal electrocoagulation process was occurred at Iron electrode (Fe as anode). For more details, the influence of time on the percentage of electrocoagulation can be seen in Figure 4 as follows:

![Figure 4. Effect of Time on Electrocoagulation percentage](image)

4.5 Effect of Electrode Distance on Electrocoagulation percentage

The electrocoagulation process is strongly influenced by the distance between the cathode and anode used in the electrocoagulation process. In the electrocoagulation process there will be a reduction reaction (at the cathode) and an oxidation reaction (at the anode). The distance between the anode and
cathode plays an important role, because this is in accordance with Coulomb's law of attractive force (if the electric charge is opposite) or reject (if the electric charge is the same). \( F = k \cdot \frac{q_1 \cdot q_2}{r^2} \) where: \( F \) is an attractive force or repulsive force, \( k \) constant and \( q_1 \) and \( q_2 \) are the magnitude of the electric charge. Optimal electrocoagulation process was occurred at 1 cM electrode distance. For more details, it can be seen in Figure 5 as follows:

4.6 Effect of temperature on the percentage of electrocoagulation
The electrocoagulation process is strongly influenced by the temperature / temperature of the reactant atmosphere. This is understandable because in the process of electrocoagulation it is strongly influenced by the movement of anions (the results of the reduction process in the cathode) and cations (resulting from the oxidation process of the anode). In the electrocoagulation process the reaction that occurs is the reaction is not spontaneous (need additional energy from the outside, in accordance with the magnitude of the E of each electrode). So it is very natural, if there is another energy addition (in this case heat energy) it will increase the rate of reduction (which occurs at the cathode) and the oxidation reaction (which occurs at the anode). Optimal electrocoagulation process was occurred at 70°C. For more details can be seen in Figure 6 as follows.

4.7 Comparison Results of Batik Wastewater before and after the Electrocoagulation Process.
The success of the electrocoagulation process can be seen from the results of the analysis of Batik Waste Water Before and After the Electrocoagulation Process. The parameters of COD, TSS, pH and Turbidity are some parameters that can be used as an embodiment of wastewater quality. The greater the price of COD, TSS, pH and turbidity means that the waste water is the worse the quality. Laboratory research data shows that the electrocoagulation process and after the electrocoagulation process, the results of COD, TSS, pH and turbidity were significantly reduced. This data gives information that the electrocoagulation process that occurs is effective and efficient. For more details, it can be seen in Table 1 as follows:

![The relationship Percentage of electrocoagulation and Distance Electrode](image-url)

**Figure 5.** Effect of Electrode Distance on Electrocoagulation percentage
Table 1. Comparison of Batik Waste Water Analysis Results before and after the Electrocoagulation Process.

| Parameter | Fe Anode | Zn Anode |
|-----------|----------|----------|
| Before    | After    | Before   | After    |
| COD       | 1000 ppm | 362.5 ppm| 1000 ppm | 418.9 ppm|
| TSS       | 708.40 ppm| 24.8 ppm | 708.20 ppm| 47.2 ppm|
| pH        | 6.5      | 7.3      | 6.4      | 7.4      |
| Turbidity | 6.1 NTU  | 2.8 NTU  | 6.1 NTU  | 2.9 NTU  |

Figure 6. Effect of temperature on the percentage of electrocoagulation

4. Conclusion
The electrocoagulation process has been employed in the previous study to treat the remazol black T. The effect of various operational parameters such as: distance between electrodes, temperature, acidity (pH) and electrolysis time. Results showed that applying optimum applied distance between electrodes at 1 cm, temperature at 70°C, at alkaline condition (pH > 10) and electrolysis time at 30 minutes. Iron and zinc use as an anode in batch reactor at the electrocoagulation process. Iron and zinc would same function, both metals can formed cations (iron as Fe$^{3+}$ and zinc as Zn$^{2+}$), as a coagulator of textile dyes. In general electrocoagulation is more effective in alkaline situations than in acidic conditions at 70°C. Electrocoagulation the maximum results were obtained (96.54% with iron anodes) and (81.65% with zinc anodes), thus iron is better used as an anode than zinc.

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