Treatment of wastewater batik by electrochemical coagulation using aluminium (Al) electrodes

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Abstract. Treatment of wastewater batik by electrocoagulation method using aluminium (Al) electrodes has been done. Electrocoagulation method was chosen for treatment of wastewater batik because it is cheap, easy and efficient waste degradation. This research was conducted using aluminium (Al) electrodes and sodium chloride as an electrolyte solution. The purity of aluminium electrode was analysis using Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). Electrochemical coagulation has been done using wastewater batik volume 50 mL with variation of time (10, 30, 50, 70, and 90 minutes), variation of voltage (5, 7, 9, 10, and 11 V), and variation of salt addition (0.5; 0.75; 1.00; and 1.25 g). Batik wastewater was analyzed before and after electrocoagulation by Spectrophotometer UV-Vis and the content of Pb was analyzed by Atomic Absorption Spectrophotometer (AAS). The research results show that optimum conditions electrolysis time, voltage and sodium chloride was 90 minutes, 10 V and 1.25 g, respectively. The results of this study showed the longer the electrolysis time, the higher the voltage, and the increasing number of salt added, then the batik waste decreased absorbance, alteration of color from black to clear yellow. The content of Pb in batik waste has decreased from 0.5844 mg/L to 0.1630 mg/L.

1. Introduction

The batik industry has produced organic wastes with large volumes, solid colors, strong odor and has a high temperature, pH, Biochemical Oxygen Demand (BOD), High Suspended Solid. This is due to the use of chemicals and dyes in the batik production process. The chemicals used include NaOH, Na₂CO₃, NaHCO₃, sulphuric acid, sulfite, nitrite, while the dyestuffs used include acid dyes, bases, direct dyes, reactive dyes, naphthol dyes, and vat dyes. Indigosol dye is often used because it produces bright colors and does not easily fade, but the water used by the laundry can cause disruption to the environment. Batik waste containing indigosol compounds is very dangerous because it can cause some health impacts. These dyes can cause skin diseases and are very harmful can result in skin cancer.

The industrial batik has produced liquid waste contains heavy metals which are hazardous wastes, which can cause damage to the environment. The existence of industrial waste can be known in the form of physical contamination, such as smelling sting, and contaminants will make the water becomes turbid. The emergence of these symptoms can absolutely be used as one of the signs of high levels of water pollution. Colored wastes arise from the use of dyestuffs that are still attached after use.
Batik industrial liquid waste directly discharged into the environment without being processed first then it can cause pollution, especially aquatic ecosystems. High temperatures will result in dissolved oxygen content or Dissolved Oxygen (DO) in declining water that will kill the organism thus disrupting the balance of the water ecosystem. In addition, organic waste will increase the nitrogen content into nitrate compounds that cause the bad smell.

Wastewater dyes processing can be done chemically, physics, and biology. Some researchers do research, processing textile waste is adsorption of methylene blue by using activated carbon [1], electrochemical oxidation [2,3,4,5]. Several studies have been done to treatment dyes waste. Chemically there are several methods of liquid waste treatment including photocatalytic reactions [6], and coagulation [7,8]. In addition, other methods are color degradation with oxidation reactions, anaerobic reactions, and photocatalysis reactions. Electrocoagulation is a simple and easy method for reducing various pollutants and pollutants, both organic and inorganic materials. In the research that has been done used aluminum and iron plate, and a combination of both. This electrocoagulation method is also able to decrease dissolved solids content, COD, and BOD.

The electrocoagulation method is an alternative method for reducing pollutants in wastewater. The multiple electrode application is done by assembling the Fe and Al electrode plates. Variations used in this study has the variation of plate number, size, voltage, and time. From the research it can be seen that electrocoagulation method of multiplexed electrocoagulation can to improve the quality of domestic batik wastewater, using the number of electrode plate effect on the improvement of the quality of domestic industrial wastewater. In addition, this electrocoagulation method can reduce the content of COD, BOD, TSS, pH and has met the water quality standard.

Liquid waste is classified as one of the main contaminants in batik industry activity. The liquid waste of this batik industry has a concentrated color and is carcinogenic, so it needs to get serious attention. This problem is caused by pollution by the textile dye is difficult to be overcome by biology (microorganism) and chemicals (coagulation and flocculant). Many researchers have been done treatment dyes wastewater using electrocoagulation [9,10,11,12,13]. Electrocoagulation method have done for textile wastewater [14,15,16,17]. The advantage of this electrocoagulation method is that it can replace the use of expensive (more economical) chemical reagents, resulting in a collection of suspended particles more durable and more easily filtered, producing cleaner water than with chemical coagulation or sedimentation, and can be used for processing waste that has high turbidity. In addition, the implementation of waste treatment by this method is quite simple and controlled rather than using chemical coagulants. Although it requires more complicated equipment preparation and greater investment, in the long run, this electrocoagulation method is very profitable.

In this paper has been the study of the treatmentof wastewater batik by electrocoagulation method using aluminum (Al) electrodes. Electrochemical coagulation has been done using wastewater batik with the variation of electrolysis time, variation of potential and variationof sodium chloride. The aluminium electrode was used as an anode and cathode has the analysis of purity using SEM-EDX. Batik wastewater was analyzed before and after electrocoagulationby Spectrophotometer UV-Vis and the content of Pb was analyzed by Atomic Absorption Spectrophotometer (AAS).

2. Experimental Section
2.1. Material and Instrumentation
The sample used is liquid waste from batik industry in Yogyakarta Indonesia. The instruments used in this study are one set of an electrolysis cell, magnetic stirrers, UV-Vis Spectrophotometers (Hitachi U-2010), SEM-EDX (Phenom TPMprox/Pro/Pure) for characterization of aluminium electrode, and Atomic Absorption Spectrometers (Perkin Elmer Pin Aade 900 T). The materials used in this research are aluminium metal, batik waste, sodium chloride, HNO₃ analytical grade, the solution of Pb 1000 ppm (Merck), and distillate water.
2.2. **Experimental Method**

2.2.1. **Electrocoagulation of batik waste with variation of electrolysis time and potential**

A total of 50 mL of batik waste was put into the beaker glass and added 0.5 g of sodium chloride. Then electrolyzed with a voltage of 5 V, using electrolysis time variations 10, 30, 50, 70, and 90 minutes. After the electrolysis was completed, the sample solution was filtered using filter paper and the filtrate was measured for absorbance by using a UV-Vis spectrophotometer. A total of 50 mL of batik waste was put into the beaker glass and added 0.5 gram of sodium chloride. Then electrolyzed with voltage variations (5, 7, 9, 10, and 11 V) using electrolysis time is 50 minutes. After the electrolysis was completed, the sample solution was filtered using filter paper and the filtrate was measured for absorbance by using a UV-Vis spectrophotometer.

2.2.2. **Electrocoagulation of batik waste using sodium chloride**

A total of 50 mL of batik waste was inserted into a beaker and added a kitchen salt with variations (0.25, 0.5, 0.75, 1.0 and 1.25 grams). Then electrolyzed with a voltage of 5 V. The time used is 50 minutes. After the electrolysis was completed, the sample solution was filtered using filter paper and the filtrate was measured for absorbance by using a UV-Vis spectrophotometer.

2.2.3. **Determination of Pb using Atomic Absorption Spectrophotometer (AAS)**

The sample has destruction before analysis using AAS. A total of 25 mL of batik waste was put into the Kjeldahl flask. The sample of batik waste was destruction using the HNO₃ solution as much as 5 mL. The solution is heated to a digestor block at a temperature of 100 °C. The solution was destructed to about 0.5 mL remaining. The solution in the cooled Kjeldahl flask is then fed into a 25 mL measuring flask and diluted with distilled water to the limit marker. The solution is shaken out to homogeneous. The sample solution was filtered through Whatman filter paper 41. The standard solution obtained had concentrations of 0.5, 1.0, 2.0 and 3.0 ppm. The sample solution and standard solution of Pb series were measured using atomic absorption spectrometers.

3. **Result and Discussion**

3.1. **Characterization of Aluminium using SEM-EDX**

Prior to the electrolysis of batik waste, the first aluminum electrode used was analyzed using SEM-EDX to identify and determine the composition of the aluminum electrode element. The results of aluminum electrode analysis with SEM are presented in Figure 1.

![SEM image of aluminium surface with magnification 10000x (A) and EDX spectra the aluminium surface (B)](image)

**Figure 1.** SEM image of aluminium surface with magnification 10000x (A) and EDX spectra the aluminium surface (B)
Figure 1A shows that based on SEM analysis result with 10000x magnification it is seen that aluminum surface morphology is not uniform. The surface of aluminum is scratched so uneven lines. Figure 1B shows the results of aluminum electrode analysis using EDX. Figure 1B shows that the aluminium has a high purity that is with the atomic concentration of the Al is 100%. In Figure 1B it appears that the peak that appears there is only one is aluminum, this means that the element content contained in aluminum metal contains only Al and no other elements.

3.2. Effect of electrolysis time to electrocoagulation of batik wastewater

Figure 2 shows the results of electrolysis of batik waste using a potential of 5 V with the addition of 0.5 g of sodium chloride, and variations of electrolysis time are 10, 30, 50, 70, and 90 minutes. Spectra analysis of batik waste results before and after electrolysis is shown in Figure 2.

![Figure 2. Spectra analysis batik waste before and after electrocoagulation with variation electrolysis time](image)

Figure 2 shows that the initial batik waste (before electrolysis) has a peak in the visible region of 400-800 nm, this is because batik waste before electrolysis is still colored and the solution is concentrated. After 10 minutes of electrolysis the color of batik waste began to degraded, then after electrolysis for 90 minutes batik waste solution became the clearest, so peak generated at 400-800 nm wavelength began to decline. In these circumstances, it can be seen in accordance with the results of the analysis of the batik waste solution still contains compounds that have a specific wavelength in the UV region (200-400 nm). Figure 3 shows that the longer the electrolysis process, the compound content in batik waste decreases, this is indicated by the lower absorbance rate produced.

![Figure 3. Image of degradation color of batik waste before and after electrocoagulation with variation electrolysis time 0-90 minutes](image)
3.3. Effect of potential to electrocoagulation of batik waste

Electrolysis of batik waste has been done using electrolysis time 50 minutes, 0.5 grams of salt, and with variations of 5, 7, 9, 10, and 11 Volt voltage. The spectra of the analysis of batik waste that has been electrolysis are shown in Figure 4.

![Spectra analysis batik waste before and after electrocoagulation with variation potential](image1)

**Figure 4.** Spectra analysis batik waste before and after electrocoagulation with variation potential

Figure 4 shows that the initial batik waste (before electrolysis) has a peak in the visible region of 400-800 nm, this is because batik waste before electrolysis is still colored and the solution is concentrated. After electrolysis done for 50 minutes, the color of batik waste starts clear, so electrolysis done for 50 minutes. In this research, electrolysis process with the variation of 5, 7, 9, 10, and 11 Volt. The results of the analysis can be seen that the electrolysis process at a voltage of 5 V causes the solution of batik waste starts clear so that the resulting absorbance lower. It can be seen that the electrolysis process influences the content of compounds in batik waste. This process can degrade the dye present in batik waste. In Figure 5 shows the color change of electrolysis result of batik waste with potential variation with electrolysis with voltage 5-11 V.

![Image of degradation color of batik waste before and after electrocoagulation with variation potential](image2)

**Figure 5.** Image of degradation color of batik waste before and after electrocoagulation with variation potential
3.4. Effect of sodium chloride to electrocoagulation of batik waste

Electrolysis of batik waste using potential 5 V, electrolysis time 50 minutes, and variation of addition of NaCl are 0; 0.25; 0.50; 0.75; 1.00; and 1.25 g. The spectra of the analyzed batik waste are shown in Figure 6.

Figure 6. Spectra analysis batik waste before and after electrocoagulation with variation of NaCl

Figure 6 shows that the initial batik waste (before electrolysis) has a peak in the visible region of 400-800 nm, this is because batik waste before electrolysis is still colored and the solution is concentrated. After electrolysis done for 50 minutes, the color of batik waste starts clear, so electrolysis done for 50 minutes. In this research, electrolysis process is done with the variation of the salt addition of kitchen 0, 0.25, 0.50, 0.75, 1.00 and 1.25 g. Based on the results of the analysis, it can be seen that when the electrolysis process without using salt peak produced began to fall and the solution of batik waste also began to clear, resulting in lower absorbance. The sodium chloride (NaCl) is a powerful electrolyte that can dissociate completely in solution into Na\(^+\) and Cl\(^-\) ions. The greater is the NaCl concentration the greater the current flowing in the solution, thus causing a greater percentage of dye degradation.

At the cathode, there will be reduction reactions to the cations, which are included in this cation are H\(^+\) ions and metal ions. The H\(^+\) ion of an acid will be reduced to a hydrogen gas that will be free as gas bubbles. Reaction: \(2H^+ + 2e \rightarrow H_2\)

If the solution contains alkali, alkaline earth metal ions, then these ions cannot be reduced from the reduced solution is the solvent (water) and hydrogen gas (H\(_2\)) formed at the cathode.

Reaction: \(2H_2O + 2e \rightarrow 2OH^- + H_2\)

The reaction on the anode used in the aluminum metal will oxidize, the reaction:

\[ Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \]
Figure 7. Electrocoagulation process on anode electrode using aluminium[18]

NaCl in the electrocoagulation process plays an important role in dye oxidation by reacting as follows [7]:

Cathode:
\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \\
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{Cl}^- + \text{HOCl} \\
\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-
\]

Anode:
\[
\text{Dye} + \text{OCl}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^-
\]

The Cl\(^-\) ion will react with water to form chlorine hydroxy, and then oxidized to form chlorine oxide and react with the dye occurring in the anode and produce CO\(_2\) gas, water, and Cl\(^-\) ions.

3.5. Determination of Pb in batik waste before and after electrolysis using AAS

Heavy metal contained in batik industrial waste is Pb. Therefore, research on the analysis of Pb content in batik waste before and after electrolysis. The absorbance of the standard solution of Pb has been obtained, then made calibration curve to be obtained by the equation. The equation is used to determine the concentration of Pb in batik waste.

The obtained line equation is then used to calculate the concentration of Pb in batik waste. The concentration of Pb in batik prior to electrolysis was 0.5844 mg/L. In the analysis of Pb content in batik waste after electrolysis, the samples used are the variation of sodium chloride, that is 0.5 g of sodium chloride with potential 5 V and electrolysis time is 50 minutes. The absorbance is then used to make the standard solution calibration curve of Pb. The calibration curve of the concentration of standard Pb solution with its uptake is shown in Figure 8.

Figure 8. The calibration curve of the concentration of standard Pb solution
The obtained line equation is then used to calculate the concentration of Pb in batik waste. The concentration of Pb in batik waste after electrolysis was 0.1630 mg/L. The concentration of Pb in batik waste water before and after electrolysis process is 0.5844 mg/L and 0.1630 mg/L so that Pb content in batik waste fulfil the maximum requirement of Pb content in water is 1.0 mg/L.

4. Conclusion
The result of characterization of aluminum (Al) with SEM EDX shows surface is no uniform with high purity is 100%. The optimum result shows that batik wastewater treatment using electrolysis time, potential and sodium chloride is 90 minutes, 10 volts and 1.25 g respectively, seen from the color of batik waste which originally dark black become yellow clear. Aluminum electrode is more economical and is a good electrical conductor. The content of Pb in batik wastewater after electrolysis decreased the concentration of 0.5844 mg/L to 0.1630 mg/L.

References
[1] Yasin 2007 The Malaysian Journal of Analytical Sciences. 11 400
[2] Nordin N, Amir S F M, Riyanto and Othman M R 2013 Int. J. Electrochem. Sci. 8 11403
[3] Nordin N, Amir S F M and Yusop M R 2015 Acta. Chim. Slov. 62 642
[4] Panizza M and Huittle M 2013 Elsevier J. 90 1455
[5] Sala M and Gutierrez B M C 2012 International Journal of Photoenergy. 10 1
[6] Rashed M N and El-Amin A A 2007 Int. J. Phys. Sci. 2 3 73
[7] Chatzisymeon E, Xekoukoulotakis N P, Coz A, Kalogerakis N and Mantzavinos D 2006 Journal of Hazardous Materials, B137 998
[8] Kobaya M, Tan O C and Bayramoglu M 2003 Journal of Hazardous Materials. B100 163
[9] Nandi B K and Patel S 2017 Arabian Journal of Chemistry. 10 2961
[10] Fajardo A S, Martins R C, Silva D R, Martinez-Huittle C A and Ferreira R M Q 2017 Journal of Electroanalytical Chemistry. 801 30
[11] Bassyouni D G, Hamad H A, El-Ashtoukhhy E S Z, Amin N K and Abdel-Latif M M 2017 Journal of Hazardous Materials. 335 178
[12] Segura S G, Eiband M M S G, Melo J V and Huittle C A M 2017 Journal of Electroanalytical Chemistry. 801 267
[13] Eyvaz M, Kirlaroglu M, Aktas T S and Yuksel E 2009 Chemical Engineering Journal. 153 1-3,16
[14] Aoudj S, Khelifa A, Drouiche N, Hecini M and Hamitouche H 2010 Chemical Engineering and Processing: Process Intensification. 49 1176
[15] Kobya M, Demirbas E and Can O T 2006 Journal of Hazardous Materials. 132 183
[16] Khandegar V and Saroha A K 2013 Journal of Environmental Management. 128 949
[17] Phalakornkule C, Polgumhang S, Tongdaung W, Karakat B and Nuyut T 2010 Journal of Environmental Management. 91 918
[18] Den W and Huang C 2005 Colloids and Surfaces A: Physicochemical Engineering Aspects. 254 81

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