Preparation of carbon-polyvinyl chloride (C-PVC) and its application for electrodes to electrochemical degradation of batik wastewater

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Abstract. Batik industrial waste contains some hazardous substance, such as Remazol Black B, Remazol Red AB, Remazol golden yellow RNL, naphthol, benzene and other azo dyes class. Batik dye also contains high Pb, COD and TDS which electrochemical degradation is needed. Preparation and application of carbon-PVC (95% w/w: 5%) electrode using the batch system for batik waste degradation with electrolysis method were performed in this study. Variations of voltage and electrolysis time used are 6, 7, 8, and 9 V and 60, 90, 120, and 150 minutes, respectively. Electrolysis was done by the addition of 1.5 g NaCl and the flow of external DC circuit Sanfix SP-303E. The optimum results were obtained from electrolysis with the voltage of 9 V in 150 minutes with 97.68% of waste degraded, and percent reduce TDS until 91.16%, total Pb metal content of 0.636 mg/L and COD figures amounted to 95.76%. This study concludes that electrolysis method using carbon-PVC electrode was used to degrade the batik waste is effective and can be reduce the value of COD, total Pb, and TDS.

1. Introduction
Batik industrial process uses natural and non-natural chemicals. The chemicals in the used dyeing process of batik cloth consist of chemical compounds harmful to health and environment. The use of dyes in high concentrations can cause new problems when processing batik waste. Problems are arising from some batik industry that is difficult to process the coloring waste result from batik industry that is poisonous and dangerous. Batik industrial waste contains some harmful dyes such as black B remazol, remazol red AB, remazol golden yellow RNL, naphthol, and organic compounds [1,2]. Batik waste contains heavy metals such as Pb, Cu, As. In addition, batik waste also has a high COD, and pH is the effect of the pH environment. If the waste is discharged into the environment without first processing, it will cause environmental pollution problems.

Textile waste has been done the treatment using chemical, physical and biological methods. Several researchers has reported methods for the treatment of textile waste by using photodegradation methods [3], absorption using active sludge [4], ozone for textile degradation [5]. The oxidation process using strong oxidizing agents such as ozone and hydrogen peroxide is better [6]. Some of the methods have disadvantages such as generating other waste in the form of mud (sludge) in large quantities, only precipitate; require a long time, so that the operational costs become more expensive and less effective and efficient. Processing was done there are some weaknesses that require expensive
chemicals, the process is difficult, not environmentally friendly and generate new waste derived from chemicals used [7].

Batik waste treatment using electrolysis method can be selected to overcome the problem of batik waste which contains organic dye. Electrolysis is one of the electrochemical fields that examines electron transfer on the surface of the electrode. This technique is environmentally friendly, the green technological of the future. Electrochemical techniques are used to treat water waste containing contaminants from organic and inorganic compounds [8]. The PVC-carbon electrodes has used in the electrochemical oxidation process on landfill leachate carried out by Mussa, et al. [9]. Some researcher have been done electrolysis for degradation of phenol [10-11], electrochemical oxidation of alcohol [12], electrochemical degradation of textile wastewater [13-14], olive oil mill wastewaters [15], and tannery wastewater [16]. C-PVC (carbon-polyvinyl chloride) electrodes can used to increase flexibility in the size, shape and the electrode strength. Carbon can be used for electrode because of its conductive and inert properties [17].

Based on this condition, this research focuses on the way of batik waste treatment by the electrochemical method by electrolysis method using PVC-carbon electrode to decrease color degradation, decrease COD number, and total Pb. The objectives of the research are determination of the optimum potential and time required to degrade batik waste using PVC-carbon electrodes. The effectiveness of electrolysis process of batik waste using PVC-carbon electrode can be seen from the color change, percent degradation, TDS, the concentration of Pb, and COD. The characteristics of C-PVC electrodes have been analysis using SEM-EDX.

2. Experimental Section

2.1. Instrumentation and materials
The instrumentation used in this research are DC power supply from Sanfix SP-303E, magnetic stirrer, analytical balance, stopwatch, pH meter, Spectrophotometer UV-Vis Hitachi U 2010, Scanning Electron Microscopy (SEM) EDX series Jeol JSM-6510 LA, and Atomic Absorption Spectroscopy (AAS) Perkin Elmer. The materials used in this research include batik liquid waste from Jaya Kusuma Batik Yogyakarta, NaCl (Merck), silver conductivity point, epoxy glue, silver wire, carbon powder (Merck), polyvinyl chloride (PVC) from Merck, tetrahydrofuran (THF) analytical grade from Merck and distillate water.

2.2. Preparation of PVC-carbon electrode
PVC-carbon electrodes used for the anode and cathode electrodes. The preparation of the carbon-PVC electrode is 95% carbon from Merck, then added grade 5% PVC powder (w/w) of 5 g total weight. The C-PVC was dissolved in 10 mL of THF solution. The mixture is stirred and allowed to stand for 24 hours. The carbon-PVC was pressed with strength is of 10 tons/cm² in the form of a tablet with a diameter of 1.3 cm. The pellet electrode was connected with a silver wire on a hollow glass rod. The PVC-carbon electrode is given a silver conductivity point when paired with silver wire. The outer layer of silver conductivity point was covered with epoxy glue.

2.3. Characterization of C-PVC electrode
C-PVC electrode was analysis using the Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX Jeol type JSM-6510 LA) for determination of morphological structures. The surface morphological was analysis on PVC-carbon electrode before and after electrolysis process with several optimum enlargements. The result of the SEM-EDX analysis is used to know the difference of surface structure of the electrode at the PVC-carbon composite electrode and to know the percentage of elements present in the PVC-carbon electrode.
2.4. Analysis of batik wastewater before and after treatment

Analysis on batik waste samples taken from the washing of batik cloth and wax. Samples of batik waste was stored in plastic bottle according to SNI procedure. Batik waste was measured absorbance with U-Vis Spectrophotometer Hitachi U-2010. Samples was analysis before and after electrolysis with parameter are pH, temperature, COD (mg/L), TDS (mg/L), total Pb. The concentration of Pb was measured by AAS Shimadzu.

Wastewater batik was electrolysis using C-PVC electrode. Wastewater batik is took as much as 50 mL and put into the electrolysis cells. The electrolysis has been done in the electrolysis cells with a batch system. The electrolysis cells was connecting by power supply is the DC Sanfix SP 303-E potential source. The electrode was used in this study is C-PVC electrode as cathode and anode. The electrode is inserted in the sample then electrolysis is run with potential variations (6, 7, 8, and 9 V).

The electrolysis process was carried out with the addition of 1.5 gram NaCl salt with electrolysis time are 60, 90, 120 and 150 minutes. The electrolysis results are stored in a glass erlenmeyer and closed tightly. The electrolysis results are the determination of the waste to known color degradation results.

2.5. COD test of batik waste before and after electrolysis

The sample was taken 2.5 mL and inserted into a closed reaction tube. The samples were added 1.5 mL of digestion solution (the mixture of K2Cr2O7 and HgSO4) and added 3.5 mL of H2SO4 solution. The sample solution was heated in a 150°C COD reactor for 2 hours then cooled under normal room temperature. Let the suspension precipitate and the clear part of the solution be measured with the UV-Vis Spectrophotometer at the specified wavelength. If the concentration of COD 100-900 mg/L does at a wavelength of 600 nm. If the concentration of COD < 100 mg/L performs at a wavelength of 420 nm. Perform titration by ferroin indicator solution with red titration point of red brown.

3. Result and Discussion

3.1. Characterization of waste water batik before electrolysis

Waste water batik with dark brownish green color taken by using plastic bottle. The plastic bottle was washed with soapy and rinsed clean with distillate water flowing according to SNI 6989.57-2008 standard. The sample was kept in the shade or away from the sun. Table 1 shows the condition of batik waste before electrolysis has alkaline pH, TDS, COD, and large Pb concentration. Waste water batik have alkaline pH, this result same with the statement by Kasam, et al. [18].

Table 1. Result of analysis waste water batik before electrolysis

| Parameters | Value       |
|------------|-------------|
| Suhu (°C)  | 28.5 °C     |
| pH         | 7.7         |
| COD (mg/L) | 11668.8 mg/L|
| TDS (mg/L) | 1443 mg/L   |
| Pb (mg/L)  | 7.2 mg/L    |

3.2. Electrolysis of waste water batik using C-PVC electrode

Figure 1 shown the color change occurs after the electrolysis process with the C-PVC electrode with the addition of NaCl 1.5 g. The results are that the color change influenced by the variation factor of the increase of electric potential and the time of electrolysis. Electrolysis at potential 9 V and 150 minutes was the result of colorless waste. The optimum condition for batik waste electrolysis occurred at potential 9 V, time 150 minutes with a decrease of TDS value of 94.73% and final pH value of 9.2.
Figure 1. Color change from waste water batik before and after electrolysis using C-PVC electrode in NaCl 1.5 g with electrolysis time 60, 90, 120, 150 minute and potential constant at (A) 6, (B) 7, (C) 8 and (D) 9 V

Measurement of waste degradation quantitatively is determined by Spectrophotometer UV-Vis Hitachi U-2010 to determine the decrease of waste absorbance before and after electrolysis. Colored compounds and organic compounds containing double bonds and chromophore groups can be analyzed using a spectrophotometer UV-Vis. Analysis have been done on wavelength visible (400-800 nm) and UV (200-400 nm). Figure 2 shown UV-Vis spectra from waste water batik before and after electrolysis using C-PVC electrode in NaCl 1.5 g with electrolysis time 60, 90, 120, 150 minutes and potential constant at 6, 7, 8 and 9 V.
Figure 2. UV-Vis spectra from waste water batik before and after electrolysis using C-PVC electrode in NaCl 1.5 g with electrolysis time 60, 90, 120, 150 minute and potential constant at (A) 6, (B) 7, (C) 8 and (D) 9 V

Figure 3 show the effect of electrolysis time to % degraded waste using C-PVC electrode at potential 9 V with various electrolysis time 60, 90, 120, and 150 minutes. The C-PVC electrode have been used for the electrolysis of waste water batik optimum at potential 9 V. Electrolysis result has been done at 60, 90, 120, 150 minutes is can to degrade waste that is 33.25, 53.34, 78.94 and 97.68%, respectively. Perfectly degraded batik waste occurs at 9 V with a time variance of 150 minutes with a percentage of 97.68% and a non-degraded residual of 2.32%. 
3.3. Effect of the electrolysis time and potential to Chemical Oxygen Demand (COD)

According to Government Regulation of the Environment No.5 Year 2014 the maximum limit of textile industry waste for COD that is allowed that is 150-350 mg/L. Waste must be treated with variations time electrolysis and potential up to clear batik waste. Electrolysis was carried out on 50 mL batik waste with electrolysis time 60, 90, 120, and 150 minutes and potentials 6, 7, 8, and 9 V. The NaCl with the concentration of 1.5 mg/L can be used for that helps speed up the decomposition of chemical compounds in batik waste.

Figure 3. The effect of electrolysis time to % degraded waste using C-PVC electrode at potential 9 V with various electrolysis time 60, 90, 120, and 150 minute

Figure 4. The effect of electrolysis time and potential to decrease of COD at electrolysis batik wastewater using C-PVC electrode
decrease COD is 150 minutes and potential 9 V. The longer the electrolysis process and the higher the potential use, the greater the values of COD decrease in batik waste. Electrolysis conducted at 9V potency with electrolysis time for 150 minutes has the best percentage to decrease COD of batik waste amounted to 95.76%. The electrolysis is an effective method for decrease of the COD in batik waste.

3.4. The effect of electrolysis time to concentration of Pb in waste water batik

Figure 5 shown effect of electrolysis time to decrease of concentration of Pb in waste water batik. Analysis of concentration of Pb on batik waste for before and after electrolysis has been done using Atomic Absorption Spectrophotometer (AAS). The result of measurement with the coefficient of determination result $R^2 = 0.999$ at a wavelength of cathode lamp that is 217 nm. Electrolysis process that flowing electrics causes the migration of Pb$^{2+}$ ions leads to the pole of the cathode. The Pb$^{2+}$ ion was can be reduced to Pb at the cathode. The reduction process on the cathode surface causes Pb to be neutral. These processes cause a decrease of concentration of Pb in waste water batik after electrolysis. Figure 5 shows the optimum time electrolysis is 150 minute can decreasing of Pb up to 0.636 mg/L with the percentage of Pb up to 91.16%.

![Figure 5](image)

**Figure 5.** The effect of electrolysis time to decrease of concentration of Pb in waste water batik

3.5. Characterization of C-PVC electrode before and after electrolysis using SEM-EDX

Figure 6A shown of surface morphology of the C-PVC electrode before electrolysis. The surface electrode was covered by vinyl chloride. The carbon was spread evenly with different sizes and coated with chlorine from the bonding with the PVC composite, so that it looks more rigid. Figure 6B shown of surface morphology of the C-PVC electrode after used for electrolysis with same magnification is 5000x. Based on SEM-EDX analysis shown on surface morphology of the C-PVC electrode is cracked and hollow surfaces. This condition is good properties for electrode because of the greater contact between the solution and the electrode. Figure 7A and 7B show the EDX spectra of C-PVC electrode before and after used electrolysis. Based on the EDX spectra shown is not the different chemical composition of C-PVC electrode before and after used electrolysis. C-PVC electrode is good stability for electrolysis of waste water batik in sodium chloride solution.
4. Conclusions

Based on the research, it can be concluded that the electrolysis method using carbon-PVC electrode is effective for degrading waste water batik at the variation of potential 9 V and electrolysis time 150 minutes. Electrolysis using the C-PVC electrode with potential 9 V and electrolysis time 150 minutes can degradation of the waste water batik of 97.68% and can decrease the TDS value to 63 mg/L, Pb of 91.16% and COD of 95.76%. Characteristics of C-PVC electrode after used electrolysis shown not change chemical composition and morphology. C-PVC electrode is the best material for treatment of waste water batik using electrolysis method.
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