Utilization of Pb and PbO$_2$ from lead storage battery waste for batik wastewater treatment using electrochemical method

Riyanto$^{1,3}$ and Siti Wulandari$^2$

$^1$Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Islam Indonesia, Jalan Kalirungan KM 14.5 Sleman, Yogyakarta, 55584, Indonesia.

$^3$e-mail: riyanto@uii.ac.id

Abstract. In this study, we developed of utilization of Pb and PbO$_2$ from lead storage battery waste for batik wastewater treatment using electrochemical method. This research aimed to degrade batik wastewater with direct oxidation in the electrolysis cell. Degradation has been done by electrolysis of 50 mL batik waste using Na$_2$SO$_4$ as electrolyte with various concentrations and voltages. The electrolysis result were analyzed by Spectrophotometer UV-Visible. The result showed that PbO$_2$/Pb electrode from lead storage battery waste has high effect for electrochemical degradation of batik wastewater. Based on UV-Visible spectrum showed that the optimum several of electrolyte concentration and voltage for degradation batik waste was 0.4 M and 9 V, respectively. As conclusions, Pb and PbO$_2$ from lead storage battery waste can be used for electrode for batik wastewater treatment using the electrochemical method.

1. Introduction

Batik production process uses a lot of chemicals that can cause environmental pollution. These chemicals are commonly used in dyeing processes. The chemicals in the process are usually dissolved in water and without removed. In general, pollutants contained in industrial batik waste other than dyes can also be heavy metals, suspended solids or organic substances.

Indigosol dye is often used because it produces bright colors and does not easily fade, but the water used can cause disruption to the environment. Batik waste containing indigosol compounds is dangerous because it can cause some health impacts. These dyes can cause skin diseases and are very harmful can lead to skin cancer. Several techniques have been done to the treatment of batik waste such as coagulation, sedimentation, adsorption and electrochemical (electrolysis). Based on the problem, it is necessary to process liquid waste from batik industry with a method that does not produce other waste, so that electrolysis method is chosen for batik waste treatment. Electrochemical methods have many advantages: not providing additional contamination to the environment, shorter processing time, able to overcome the liquid waste of batik industry with satisfactory results and do not require a lot of complicated analytical process [1-3].

The main factors that support the success of the electrolysis process are electrolytes and electrodes. Several studies have been used NaCl and Na$_2$SO$_4$ electrolytes because of good electrical current, and able to degrade batik waste. Research conducted Ariguna et al. [4] electrochemical degradation of Remazol Yellow FG by electrochemical oxidation technique obtained result indicating that the use of NaCl as the electrolyte has high efficiency. Na$_2$SO$_4$ is good electrolyte for electrolysis of dye at 8 V
using PbO$_2$/Pb electrode. Sample solution was added 0.71 g Na$_2$SO$_4$ able to electrochemical decolorize of indigosol and black B remazol dye of 98.02% and 99.42%, respectively [5].

Widodo et al. [6] have conducted research on the use of PbO$_2$/Pb and PbO$_2$/carbon as electrodes for electrodecoloration of black B remazol solution. PbO$_2$/Pb electrode effective result in electrochemical destruction process of black B remazol dye compared to PbO$_2$/carbon electrode. At room temperature, the electrochemical decolorization of black B remazol samples using the PbO$_2$/Pb anode has lasted 100% to CO$_2$, H$_2$O and short chain carbon compounds and has no chromophore (color-giving) groups. The electrochemical decolorization using PbO$_2$/carbon has completely the dyestuff and leaves a benzene-ring compound which can be removed well with the addition of electrolysis time. Lead dioxide as an electrode selected taking into account the nature of this material in electrolysis, stable and electrocatalysis effect is expected to provide synergies in remediation polluted waters with the electrochemical approach.

Batik waste water has treatment by using Pb electrode, as in the research conducted on the degradation of Remazol Brilliant Blue in fabric woven waste by electrocoagulation method starting with the determination of maximum wavelength and calibration curve determination, to determine pH, current strength and contact time. Several studies of the removal of color and organic compounds present in batik industrial wastewater have been carried out, for example by chemical means such as color degradation with oxidation reactions, anaerobic reactions and photocatalysis reactions [7]. In the previous research, the electrolysis method (electrochemical decolorization) was chosen as one of the alternative treatment of dye waste. The advantage of this method compared to other methods is effective and simple [8]. One of the factors supporting the success of the electrolysis process is the electrode used [9].

The use of lead oxide as an anode can overcome all problems in dye waste processing [10]. Lead dioxide has been widely used as an electrode in various studies, among others as electrodes in the oxidation of CN-ions, oxidation of sulfuric acid, and oxidation of organic wastes [11]. Based on the nature of lead dioxide which can transmit current and is inert, this material can be eligible to be electrode so that in this research selected lead dioxide anode.

Several studies have applied electrochemical methods to treat dyestuff waste with several types of electrolytes such as the Na$_2$SO$_4$ electrolyte used in the comparison of the use of two boron-doped diamond anodes and TiRuO$_2$ and as a cathode both using stainless steel [12,13]. Electrochemical degradation of the acid green dye in the electrolyte of NaCl using PbO$_2$ electrode has been done research by Ghalwa and Latif [14,15]. In this study selected PbO$_2$ electrode as the anode and Pb as the cathode by utilizing used battery. The PbO$_2$ electrode is chosen as an anode because it is a stable or non-oxidation electrode so that in the electrolytic cell undergoing a redox reaction is an electrolyte.

2. Experimental Section

2.1. Materials and chemicals

The materials used in this research are batik waste, PbO$_2$/Pb plate from used battery (lead storage batteries), distilled water, Na$_2$SO$_4$ and NaCl. This research used the chemicals were produced by Merck with grade pro analysis. Figure 1 shown used battery and PbO$_2$/Pb plate from used battery. The electrode used in the electrolysis process is PbO$_2$ in the anode and Pb in the cathode, the plate used as the electrode is the plate obtained from the motor vehicle battery.
2.2. Waste water batik Electrolysis Using PbO₂ and Pb electrode

Waste water batik is used in this research from of batik home industry in Yogyakarta. Added 50 mL sample solutions with the variation of electrolyte are NaCl and Na₂SO₄. The concentrations used in the variations of the two electrolytes were 0.2, 0.3 and 0.4 M. The solution was electrolyzed at 9 and 10 volts for electrolysis time is 3 hours. After the electrolysis of the sample is continued by filtration and transferred into the sample bottle. The analysis included color observation and absorbance measurements with Spectrophotometer UV-Visible from Hitachi U 2010. Figure 2 shows a schematic of the electrolysis cell for batik wastewater treatment using PbO₂ and Pb as anode and cathode, respectively. If the position of the electrode is reversed between the anode and the cathode, the electrolysis process cannot take place, since there is no electric current flowing on the cathode and anode.
3. Result and Discussion

3.1. The effect of NaCl to electrolysis of batik wastewater treatment

Figure 3 shows the effect of NaCl concentration to electrolysis of batik wastewater using PbO$_2$ and Pb electrode. Figure 3A shows the effect of NaCl concentration to electrolysis of batik wastewater using PbO$_2$ and Pb electrode at the potential constant is 9 V with electrolysis time 3 h. Figure 3B shows the effect of NaCl concentration to electrolysis of batik wastewater using PbO$_2$ and Pb electrode at the potential constant is 10 V with electrolysis time 3 h.

![Graph A](image1)

![Graph B](image2)

**Figure 3.** UV-Vis spectra from electrolysis of wastewater batik using PbO$_2$/Pb electrode electrolysis time 3 h with various concentration of NaCl at potential constant 9 V (A) and 10 V (B)

Figure 3 shows the result of degradation of batik waste before electrolysis and after electrolysis can be seen from UV-Vis spectrum at wavelength 200 nm to 800 nm. The electrolysis with the variation of NaCl concentration added to the solution to be electrolyzed. The electrolysis results show a good variation in NaCl concentration of 0.4 M and there is a peak showing the presence of unconjugated benzene with other double bonds. It proves that batik waste electrolysis has taken place and removed the color perfectly but still leaves a short chain carbon compound and does not have a chromophore (color-giving) group.
The effect of NaCl on electrolysis is in the role of NaCl as a good conductor of electricity and can degrade batik waste during the electrolysis, so that the result absorbance gets smaller with the added concentration NaCl added to the waste in the electrolysis process. According to Mussa et al. [16] possible reactions to electrolysis waste water batik using NaCl electrolyte:

\[
\begin{align*}
\text{Anode (+:)} & : \quad \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \\
& \quad 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \\
& \quad \text{Cl}_2 + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OCl}^- + \text{Cl}^- \\
& \quad \text{Dye} + \text{OCl}^- \rightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} \\
\text{Cathode (-):} & : \quad 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- 
\end{align*}
\]

**3.2 The effect of Na\textsubscript{2}SO\textsubscript{4} to electrolysis of batik wastewater treatment**

Figure 4 shows the electrolysis result with the variation of Na\textsubscript{2}SO\textsubscript{4} concentration added to the solution to be electrolyzed. Electrolysis has been done using Na\textsubscript{2}SO\textsubscript{4} as electrolyte solution with electrolysis time and potential constant is 3 hours and 9 V (Figure 4A).

![Figure 4A](image)

![Figure 4B](image)

**Figure 4.** UV-Vis spectra from electrolysis of wastewater batik using PbO\textsubscript{2}/Pb electrode electrolysis time 3 h with various concentration of Na\textsubscript{2}SO\textsubscript{4} at potential constant are 9 V (A) and 10 V (B).

Figure 4B shows the electrolysis waste water batik using Na\textsubscript{2}SO\textsubscript{4} as electrolyte solution with electrolysis time and potential constant are 3 hours and 10 V. Figure 4 shows that there has been a decrease in absorbance of batik waste after electrolysis. It can be seen from the picture that batik waste before electrolysis that the absorption peak at 680 nm identified the chromophore group color character in batik waste with the absorbance of 9.752 and after electrolysis for 3 hours with 9 V in Na\textsubscript{2}SO\textsubscript{4} 0.2 M its absorbance rises to 10 at a wavelength of 222 nm. The electrolysis results show a
good variation of Na$_2$SO$_4$ concentration of 0.4 M and there is a peak indicating the presence of unconjugated benzene with other double bonds. It proves that batik waste electrolysis has taken place and removed the color but still leaves a short chain carbon compound and does not have a chromophore (color-giving) group.

![Figure 5](image)

**Figure 5.** Degradation of color of batik waste water (50 mL) after electrolysis at potential constant (A) 9 V and (B) 10 V using NaCl with various concentration (1) 0.2 M, (2) 0.3 M and (3) 0.4 M electrolysis time 3 h

Figure 5 shows the color changes that occur in the degradation process of batik waste. The effect of voltage can be seen in Figure (5A) with 9 V for electrolysis time 3 hours with the variation of NaCl concentration 0.2, 0.3 and 0.4 M experiencing color change significantly. The color of the resulting electrolysis solution is much different from the color of batik waste before electrolysis. The fine powder is probably the residual lead sulfate (PbSO$_4$) that is still attached to the plate. However, the result of electrolysis that has filtered indicates the perfect degradation of batik dye waste. From Figure (5B) with a voltage of 10 V for electrolysis time 3 hours on a variation of NaCl concentration of 0.2, 0.3 and 0.4 M underwent significant color changes. The color of electrolysis solution obtained much different from the color of batik waste before electrolysis, the solution after the electrolysis process must be filtered first because there is still a fine powder marked with a turbid color. However, the color of electrolysis results at 10 V is not a good as the result of electrolysis of 9 V. Base on this data can be concluded, that the higher the voltage the easier the degradation of batik waste.
Figure 6. Degradation of color of batik waste water (50 mL) after electrolysis at potential constant (A) 9 V and (B) 10 V using Na$_2$SO$_4$ with various concentration (1) 0.2 M, (2) 0.3 M and (3) 0.4 M electrolysis time 3 h

Figure 6 shows the color changes that occur in the degradation process of batik waste. The effect of voltage increase can be seen in Figure (6A) with potential 9 V for electrolysis time 3 hours on the variation of Na$_2$SO$_4$ concentration 0.2, 0.3 and 0.4 M experiencing significant color change. The color of the electrolysis solution obtained much different from the color of batik waste before electrolysis, the solution after the electrolysis process must be filtered first because there is still a fine powder but not so visible. The fine powder is probably the residual lead sulfate (PbSO$_4$) that is still attached to the plate. However, the result of electrolysis that has filtered indicates the perfect degradation of batik dye waste. From Figure (6B) with potential 10 V for electrolysis time 3 hours at the variation of Na$_2$SO$_4$ concentration 0.2, 0.3 and 0.4 M experienced significant color change. The color of electrolysis solution obtained much different from the color of batik waste before electrolysis, the solution after the electrolysis process must be filtered first because there is still a fine powder. However, the fine powder of the electrolysis at 10 V is not as much as the electrolysis of the 9 V. Base on this data can be concluded that the higher of potential is more effective for electrochemical degradation of the batik waste. This electrolysis process produces black mud on the use of NaCl electrolyte attached to the PbO$_2$ anode, it shows a change in the PbO$_2$ anode with the addition of a black coat attached to the plate. The change of the electrode surface of PbO$_2$ anode can be seen on Figure 7.
Figure 7. Characterization of electrode surface (A) PbO$_2$ anode before used electrolysis and (B) after used electrolysis

Figure 7 shows an apparent change in the PbO$_2$ anode, during which electrolysis occurs attachment of the sludge lining the PbO$_2$ causing the PbO$_2$ not used for subsequent electrolysis. The coating attached to the anode causes an inhibition of the flow of electric current, so that the electrolysis process does not take place. The electrolysis process results in sludge when using a NaCl electrolyte in the form of black mud and when using a Na$_2$SO$_4$ electrolyte in a purplish blue mud. The weight of the PbO$_2$ anode after electrolysis increased from the weight before electrolysis. One of the PbO$_2$ plates used during electrolysis using a 0.2 M NaCl at potential 9 V with an anode weight of PbO$_2$ before electrolysis 9.2363 g then changed to 9.754 g. On the cathode plate that has used for batik waste water electrolysis, there is a visible reduction of the weight of the eroded electrode but has not changed significantly. The cathode plate is reused for electrolysis batik waste do not show good results, caused by the low current does not even produce a current at all so that the electrolysis process is not the success. The results are not maximal is seen from the solution of the electrolysis is still dark and when filtered to produce a little mud, then the organic degradation process of organic compounds occur is not maximal.

4. Conclusions
The effect of electrolyte on batik waste electrolysis is Na$_2$SO$_4$ better than NaCl electrolyte. The effect of potential on batik waste electrolysis is the higher the potential, the more easily decomposed the compound of color substance. PbO$_2$/Pb electrode from used batteries can degrade batik waste dye compound with the best electrolyte Na$_2$SO$_4$ at 0.4 M concentration with potential constant 9 V. The effect of electrolysis on the electrode shows that the mud lining the anode and the cathode plate erode. The erosion properties of the PbO$_2$/Pb electrode are not significant. The conclusion is that PbO$_2$/Pb electrode is very suitable for electrochemical degradation of waste water batik.
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