Electroremediation of Polluted Water: Electrodecolorization of Batik Wastewater

Didik Setiyo Widodo\textsuperscript{a}, Abdul Haris\textsuperscript{a}, Gunawan\textsuperscript{a}

Abstract
Research on decolorization of batik wastewater sampled in Buaran, Pekalongan, Central Java, Indonesia has been done. The research was performed by electrolysis approach. Samples of unknown dye contents were electrified in constant electrical potential of 4.5 V within 2 hours, in a single chamber with two electrodes, Pb as cathode and PbO\textsubscript{2} as anode. The purposes are to eliminate the colour of the batik wastes and decreasing its COD, TSS and TDS value as well. Samples were evaluated in the environmental parameter’s values before and after treatment quantitatively and analysed qualitatively by UV-Vis spectrometer. Results show that the method decolourize the batik waste up to 95 \%, while decreasing COD, TSS, and TDS values as much as 93.7 \%, 99.7 \% and 99.4 \%, respectively. Besides, pH samples were maintained at safe level.

Keywords: Electrodecolorization; dye; batik waste; Pb/PbO\textsubscript{2}

\textsuperscript{a}Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University Semarang, Indonesia

Corresponding author e-mail address: didie_chem@yahoo.com

Introduction
Batik production linked to water pollution due to its dye organic macromolecular content used in dying process. The polluted water unsupport the life of aquatic ecosystem anymore. Kobya, et al (2003) has been identified waste of dying and finishing process with COD value over 1600 mg/L as a harmful water (high strength wastewater). The water gives bad impact to environmental damage significantly. Moreover, several areas in Indonesia, like Pekalongan, Central Java, has developed batik as an outstanding indigenous product of home industry supported fully by regional and national authority. in the city, the waste is one chronicle problem, instead, related to aesthetical aspect as worst as water colour, bad odor, and silting and constriction of river base. Dye molecules also affect bacterial growth and covering the sunlight to penetrate in and reducing photosynthesis (Allen and Koumanova, 2005). The problems need to be overcome.

Some efforts have been conducted chemically, biologically, physically, and photocatalytically (Rashed and El-Amin, 2007; Mondal, 2008; Mazmanci and Unyayar, 2005). An alternative method that is purposed to increase the effectiveness of water remediation, namely electrodecolorization utilizing chosen electrode have been reported by former researchers, as well as Szpyrkowicz et al (2001), Roesslera et al (2001), Carneiro et al (2003), Esteves and Silva (2004), Huitle and Ferro (2006), and Gupta et al (2007) did with electrochemical approach. Electrochemical base process successfully eliminated substances contained in industrial wastes (Vlyssides et al, 2001; Tsai et al, 1997, Zhao et al, 2014(a), Zhao et al, 2014(b), Tian et al, 2013). This research utilize material of used accumulator as electrode. The material PbO\textsubscript{2}, is expected to synergistically increase the effectiveness of electrodecolorization in degrading dye of the batik waste. The aims of this research are to decolourize batik’s liquid waste by electrolyzing sample using PbO\textsubscript{2} electrode and decreasing environmental parameters of dye-polluted aquatic including pH, COD, TSS, and TDS that in turn contribute in providing clean aquatic free from dye pollutant.

Methodology
Materials used are samples of batik waste taken from Buaran Pekalongan (Central Java), Na\textsubscript{2}SO\textsubscript{4}(p.a), concentratedH\textsubscript{2}SO\textsubscript{4}, Pb and PbO\textsubscript{2} of used accumulator, while electrolysis was performed in a cell equipped with power supply and multimeter. Sample analysis was conducted by UV-vis spectrometer (Shimadzu). Solutions before and after treatment were also analysed quantitatively to measure its pH, COD, TSS and TDS.

The project was initiated by performing preliminary experiments to obtain application potential. It was carried out by electrolyzing solvent system and sample solution over varied potential. Current occurred was plotted against varied potentials to find its turning point of the graph. It indicates the change of current.
rate that is defined as decomposition potential point. by the point, application potential was determined. Samples decolorization was performed by applying the application potential to sample solution within 2 hours which is time determined before. Before and after treatment, samples were evaluated in some environmental parameters as well as its uv-vis spectra of the dye.

**Results and Discussions**

Preliminary experiments result in value of application potential and fact that the method is effectively destruct dye sample by decreasing the intensity of solution colour as well as depicted in figure 1 and 2 below. Figure 1 describes us the potential point at which redox process come to initiate. Then, figure 2 infers that the treatment take 90 minutes to decolourize dye up to 95 % and 2 hours to complete more than 99 % decolourisation.

Electrolysis of the sample result in transparent solution. The clearness was evaluated by measuring its absorbance spectrometrically. UV-Vis spectra of sample, before and after treatment was provided in the following figure.

Figure 1. Electrolysis of sample and blank solution at varied applied potential

**Figure 2. Decolourisation of dye sample using PbO₂ anode**

The former studies enable us to continue discussion on decolourisation of batik waste to be clean aquatic system. Sample took from residual liquid of dying process and river water flowing onto the city was then treated with the same method. Sample electrolysis was performed at potential of 4.5 V within 2 hours. The potential is a minimum energy as high as energy required to destruct the dye solution electrochemically. Process was conducted at single compartment equipped with Pb as cathode and PbO₂ as an anode electrode. PbO₂ is expected will do the synergistic effect during electrolysis. The phenomenon related to the catalytic aspect of PbO₂ sensitized with electric energy during electrolysis. This consideration will be discussed later.

Electrolysis of the sample result in transparent solution. The clearness was evaluated by measuring its absorbance spectrometrically. UV-Vis spectra of sample, before and after treatment was provided in the following figure.

**Figure 3. UV-Vis spectra of waste sampled from residual process (a) and river water (b) of Buaran Pekalongan before treatment**

Figure 3 describes that batik waste contain some dyes that specifically unknown. There are also no previous researches available reporting any kind of dyes contained in the Buaran batik wastes. It is difficult to cite a specific dye due to the samples are completely unknown. But, it is supposed to be remazol black B, naphtol group, and alizarin are occurred within the samples, as local batik practitioners says. Moreover, wastes that has been discharged to river become more complex solution system. Considering the figure 3, dyes contaminating the river contain many functional group including OH-substituted benzene chain as indicated as 226 nm and 277 peaks. If it were a naphtol, it will be difficult to destruct. Peaks occur after 400 nm — 523 and 535 nm reveal the colour of the dye due to its chromophore group that is conjugated in some extents to make the colour permanent. by the electrolysis the bond system is deformated to CO₂ and H₂O, dyes are destructed and the solutions (waste
samples) become decolourized. This electroremediation system is effective in destruction of the dyes remaining aquatic system to be cleaner. The effectiveness is elevated by the role of PbO$_2$ used as anode.

PbO$_2$ as semiconductor material reveals its catalytic properties after sensitizing it by UV irradiation (Li et al., 2006). In this research sensitization is achieved by exposing it to an electrical energy during electrolysis. Electrolysis give more energy that is high enough to initiate the material to perform its catalytic activity. By this way the mode is called electrocatalysis. The use of PbO$_2$ make decolourisation occurs faster due to two mechanisms run in one treatment. Firstly, electrolysis of the sample itself, and secondly is electrocatalysis.

Electrocatalysis initiates with formation of $^{\cdot}$OH radicals after the sensitization step. The $^{\cdot}$OH species radically attacks dye molecules in arbitrary possible way result in intermediate more and more. Former researchers issued some way to understand the radical reaction, though by another sensitizing method. Li et al., 2006 proposed reaction scheme as follow.

Radical $^{\cdot}$OH attack organic substrate that result in another radical species. In a complete reaction, oxidation forms CO$_2$ and H$_2$O. The sustainability of the reaction is achieved by electrical energy supplies continuously. Moreover, these $^{\cdot}$OH have high oxidation potential (2.8 eV). It can attack and destruct organic compounds towards water and carbon dioxide, i.e. mineralization (Shu et al., 2004; Levec, 1997). Consequently, the waste become colourless with good properties.

$$\text{PbO}_2(\cdot) + \text{H}_2\text{O} \rightarrow \text{PbO}_2(\cdot^{\cdot}\text{OH}) + \text{H}^+ + \text{e}^-$$

$$\text{PbO}_2(\cdot) + \text{H}_2\text{O} \rightarrow \text{R}^{\cdot} + \text{H}^+ + \text{e}^-$$

$$\text{R}^{\cdot} + \text{H}^+ + \text{e}^- \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} + \text{another side product}$$

Table 1. Data on COD, TSS, TDS, pH measurement before (1) and after (2) treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>COD</th>
<th>TSS</th>
<th>TDS</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td></td>
</tr>
<tr>
<td>River Water</td>
<td>319.48</td>
<td>26.6</td>
<td>7.17</td>
<td>1.99</td>
</tr>
<tr>
<td>Residual water</td>
<td>827.68</td>
<td>52.10</td>
<td>630.0</td>
<td>2.03</td>
</tr>
</tbody>
</table>

According to table 1 and considering official regulation no. 82 year 2001 (BAPPEDAL, 2002) water pH allowed to 6.0–9.0 and this sample coincide with the regulation and electrolysis do as well. Chemical oxygen demand (COD), total suspended solid (TSS), total dissolved solid (TDS) are also in good level. The environmental parameter reach the percentages of 93.7, 99.7 and 99.4 % diminish in COD, TSS, and TDS, respectively.

Figure 4 below provides us UV-Vis spectra of the waste after electrolysis. As looked, peaks related to any group disappear. It’s mean that long chain organic matter has been destructed toward short chain, like CO$_2$ and H$_2$O that environmentally benign. Data from figure 3 and 4 lead the changes in colour intensity that quantitatively reach 95 % within 90 minutes and 99 % after 2 hours.

Scheme 1. Radical $^{\cdot}$OH formation at the surface (sign [ ] ) of the electrode and attacking route toward dye substrate, R

Figure 4. UV-Vis spectra of batik waste (a) and river water (b) of Buaran Pekalongan after treatment
Conclusion

Electrolysis with PbO₂ anode might decolourize “Buaran” batik waste up to 95 % within 90 minutes or even 99 %, while decreasing COD, TSS, and TDS values as much as 93.7 %, 99.7 % and 99.4 %, respectively. Besides, pH samples were maintained at safe level.

Acknowledgements

This work was fully supported by DIPA FSM Undip, grant number: 0696/023-04.2.16/13/2011, December 20, 2011 with MAK code: 4078-27-525119, coincide with Assignment MoU of Lecturer Research at Department of Chemistry FSM Undip no. 200/N7.3.8/PL/2011, 14 April 2011

References


Presentation Discussion

Questions from:

✓ UMS participant: How come from the graph I vs potential, do you come to conclusion that Applied potential is 4.5 V?

✓ Thailand participant: (a) What is blank solution used in the research? The conductivity is low! (b) How do you come to conclusion that the product are CO\textsubscript{2} and H\textsubscript{2}O?

Answer:

✓ UMS participant: The data is concluded personally, but is still based on what potential decomposition is. It is defined by considering the rate of electrolysis but not too much potential needed, because the overpotential make the electrolysis take a complicated way. Basically, find decompositional potential, then add several volt to ensure the electrolysis occur more rapid.

✓ Thailand participant:

a. Yes, to enhance the conductivity we use a supporting electrolyt, fresh water from Buaran as solvent. After addition of the supporting electrolyt (a little bit of Na\textsubscript{2}SO\textsubscript{4} the water used as a blank.

b. The final product of organic oxidation are CO\textsubscript{2} and H\textsubscript{2}O, there are no more. So the inferential remark come from the convincingly energy supplies that are much more enough to oxidize any organic matter it is supported by another datas, like UV-vis spectra, GC an the existence of radical OH that producing more energy supplies as mus as 2.8 eV.