Reuse of dye wastewater through colour removal with electrocoagulation process

Khanittha Charoenlarp* and Wichan Choyphan

Rajamangala University of Technology Krungthep, Nang Linchee Road, Bangkok 10120 Thailand.

*Author to whom correspondence should be addressed, email: Khanittha.C@rmutk.ac.th

This paper was originally presented at the International Conference on the Role of Universities in Hands-On Education, Chiang Mai, Thailand, August 2009.

Abstract

Clean technology has become an important concern for every industry. Especially in textile dyeing factories, there is much use of water, energy, dyeing colours and chemicals. This can cause significant water and air pollution problems. Importantly, these industries might not meet priority requirements and regulations. Water is becoming a scarce commodity in many countries of the world and more attention is now being given to better water management and recycling. It is desirable therefore for environmental and economic benefits to reuse dye wastewater to prevent any pollution resulting from factory operations. This research studied the reuse of dye wastewater by removing the colours using the electrocoagulation process. Specifically, it sought to find out factors which had influence on the efficiency of the colour removal and the extent to which the dye wastewater treated with this method could be reused in the production process. Experiments were carried out on a laboratory scale on two types of dyes, namely, reactive dye and basic dye, with a variation of two types of electrode, namely, aluminum and iron. It was found that the electrode materials had influence on the dye removal efficiency. The aluminum electrode with 20 volts and 180 minutes of electrolysis was efficient in removing 96.05% of reactive dyes and 35.18% of dissolved solids, while the iron electrode with 25 volts and 180 minutes of electrolysis could reduce almost 85.61% of basic dye, 30.67% of dissolved solids, 66.67% of suspended solids, 20.61% of turbidity and 79.51% of COD. In addition, it was found that the quality of the basic dye wastewater treated by the electrocoagulation method was significantly better than that normally treated at factories by aerated lagoon and oxidation processes in most of the parameters, except the pH of solution. However, the quality was not better than the water normally used in the operating process in most of the parameters except hardness. The findings indicated that it may be possible to reuse dye wastewater treated by electrochemical process if turbidity and suspended solids are removed by filtration process.

Keywords: clean technology, textile, reactive dye, basic dye, electrolysis, Thailand
Introduction

The textile industries can be divided into drying processes and wet processing from a standpoint of water usage. The drying process uses a small amount of water and contributes an insignificant load to wastewater generation. On the other hand, the wet processing involves many operations such as preparation, dyeing, printing and finishing which consume large quantities of water and is, therefore, the major source of textile industry wastewater.

Wastewater from dyeing and finishing processes in the wet process constitute a substantial source of pollution which exhibits intense colour, high chemical oxygen demand, fluctuating pH and suspended particles. Indeed, the textile industry utilizes about 10,000 pigments or dyes and most of them are toxic substances considered dangerous to human and aquatic life [1]. According to Daneshvar et al. [2], 15% of the total world production of dyes is lost during the dyeing process and is released into the textile effluents. They must therefore be treated before final discharge to achieve legal and discharge standards. The reuse of wastewater has become an absolute necessity. Demands for the cleaning of industrial and domestic wastewater to avoid environmental problems, and especially contamination of pure water resources, are becoming national and international issues.

Many techniques have been used for treatment of textile wastewater, such as adsorption, biological treatment, oxidation, coagulation and/or flocculation. Coagulation is one of the most commonly used techniques. Inorganic coagulants such as lime and salts of iron, magnesium and aluminum have been used over many years. In coagulation operations, a chemical substance is added to an organic colloidal suspension to cause its destabilization by the reduction of forces that keep them apart. It involves the reduction of surface charges responsible for particle repulsions. This reduction in charge causes flocculation (agglomeration). Particles of larger size are then settled and clarified effluent is obtained. However, this technology usually needs additional chemicals which produce a huge volume of sludge [3, 4]. Water treatments based on the electrocoagulation technique have been recently proved to circumvent most of these problems, while being also economically attractive [5].

Electrocoagulation is an electrochemical method of treating polluted effluent whereby sacrificial anodes (aluminium or iron electrodes) corrode to release active coagulant precursors into the solution. These molecules produce insoluble metallic hydroxide flocs which can remove pollutants by surface complexation or electrostatic attraction [6]. The use of electrocoagulation for the treatment of wastewater has been reported by various authors. A literature survey indicated that electrocoagulation is an efficient process for different types of waste, e.g. soluble oils, liquids from food, textile industries and effluents from the paper industry [7, 8]. Carneiro, et al., studied the chemical and electrochemical degradation of reactive blue 4 dye (RB4 dye). It was compared using electrochemical reduction and oxidation at reticulated vitreous carbon electrode (RVC) and Ti/SnO$_2$/SbO$_x$ (3%mol) electrodes. The reduction of RB4 dye at -0.6 V on RVC electrode results in 50% of colour removal and up to 64% of TOC removal. The direct oxidation of RB4 dye at +1 V on RVC promotes only the oxidation of the amine group and there is thus no colour removal. On SnO$_2$ electrode, 58% TOC was removed and the decolourization was around 100% after 1 hour of electrolysis at 2.4 V which indicated good efficiency [9]. Chen, et al., reported that electrochemical oxidation had a high removal (89.8% efficiency) of the chemical oxygen demand (COD) of the wastewater while the membrane filter could almost totally remove the
total suspended solids (TSS) (nearly 100% reduction) and turbidity (98.3% elimination). The treated water can be reused in many production areas of the textile factory [10]. Can, et al, studied the decolourization of reactive dye solutions by electrocoagulation using aluminium electrodes. They reported that aluminium hydroxypolymeric species formed during an earlier stage of the operation efficiently remove dye molecules by precipitation, and in a subsequent stage, Al(OH)₃ flocs trap colloidal precipitates. The decolourization efficiency is due to the parameters of water, such as conductivity, initial pH and dye concentration [11].

Electrocoagulation (EC) is an attractive method for the treatment of various kinds of wastewater, by virtue of various benefits including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness [12, 13, 14]. This process is characterized by simple equipment, easy operation, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals and decreasing amounts of precipitate or sludge which rapidly forms sediments. In particular, the main benefits of this process involve the reduction of sludge generation, the minimization of the addition of chemicals and little space requirements due to shorter residence time, especially when EC compared to coagulation treatment.

This study focuses on the improvement of treatment for the wastewater generated by an acrylic textile industry located in Bangkok, Thailand. This industry produces acrylic yarn and the wastewater generation is 50 m³/day. The aim of this work was to study the factors influencing the effectiveness of textile wastewater treated by electrochemical process and the feasibility to reuse water after treatment.

Research Methodology

The electrocoagulation process was conducted in a reactor of volume. The overall experimental set up mainly consisted of a cell unit.

Electrocoagulator

The electrocoagulator was made of acrylic with the dimensions of 130 mm. x 250 mm. x 160 mm. Al and Fe electrode materials were used as sacrificial electrode in parallel mode. Both aluminium and iron cathodes and anodes were made from plates with dimensions of 45 mm. x 53 mm x 3 mm. and the space between electrodes was 100 mm. The electrodes were placed in 4000 ml of dye wastewater and connected to a digital dc power supply (Topward 6306D; 30V, 6A) operated at galvanostatic mode. The EC reactor is operated in batch mode.

Materials

Spent dye bath samples were collected from textile manufactures in Bangkok, Thailand.

Methodology

The efficiency of the electrocoagulator was studied in batch mode. Samples were treated using an electrolytic cell. In every run, 4000 ml of dye wastewater was treated and then, all samples were allowed to settle for 30 minutes in the vessel before any analysis. At the end of each run, the electrodes were washed thoroughly with water to remove any solid residues on the surface and dried. The effect of three electrochemical factors: electrode materials, electrical potential and electrolysis time on the colour removal efficiency were investigated with five replicates.
Analytical method
The effects of relevant wastewater characteristics such as pH, conductivity, turbidity, total dissolved solids and COD removal efficiencies were studied. The electrical potential was held constant for each run, being varied over the range 5-30 volts. The pH, conductivity and turbidity of the solutions were measured by pH meter (Cyberscan2500), conductrometer (Cyberscan500) and nephelometer (Jenway) respectively. COD and total dissolved solids measurements were according to the Standard Methods for Examination of Water and Wastewater [15]. The calculation of colour, turbidity, total dissolved solids and COD removal efficiencies after electrocoagulation treatment were performed using the following formula [9].

\[
CR (\%) = \frac{(C_0 - C)}{C_0} \times 100
\]  

(1)

Where \(C_0\) and \(C\) are concentrations of wastewater before and after electrocoagulation.

Results and Discussion

Effect of operational parameters

Effect of electrode materials
In any electrochemical process, electrode material has significant effect on the treatment efficiency. Therefore, appropriate selection of the electrode material is important. The electrode material for treatment of water and wastewater should also be non-toxic to human health and environment. Iron and aluminium were chosen as electrode materials because these are non-toxic and easily available. To investigate the effect of electrode materials on the colour removal efficiency, the electrocoagulation process was carried out using iron and aluminium electrodes. Figure 2 shows the colour removal efficiency against electrical potential applied to the electrodes in the electrocoagulation process.
The results indicated that for reactive dye, the aluminium electrode was more effective than the iron electrode in every electrical potential at 30 volts, which can reduce reactive colour by 93.38%. For basic dye, the iron electrode was more effective than the aluminium electrode in every electrical potential at 30 volts, which can reduce basic colour by 90.08%. From these results, it was found that, if the wastewater characteristics were different, this warranted the use of a different electrode was as well. According to Kim, et al, who studied dispersed and reactive removal by electrocoagulation process, it was reported that the electrocoagulation process was effective but that the effectiveness depended on dye type [3].

The different electrode materials had an effect on the effectiveness of water treatment because of its mechanisms.

Aluminium upon oxidation in an electrolytic system produces aluminium hydroxide, Al(OH)n where n= 2 or 3 [16]:

Anode:
\[
2\text{Al}(s) \rightarrow 2\text{Al}^{3+}(aq) + 6\text{e}^- \quad (2)
\]
\[
2\text{Al}^{3+}(aq) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Al(OH)}_3(s) + 6\text{H}^+(aq) \quad (3)
\]
Cathode:
\[
6\text{H}^+(aq) + 6\text{e}^- \rightarrow 3\text{H}_2(g) \quad (4)
\]
Overall:
\[
2\text{Al}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Al(OH)}_3(s) + 3\text{H}_2(g) \quad (5)
\]
Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe(OH)n where n = 2 or 3. Two mechanisms have been proposed for the production of Fe(OH)n [16]:

Mechanism 1: (acidic medium)

Anode:
\[
4\text{Fe}(s) \rightarrow 4\text{Fe}^{2+}(aq) + 8\text{e}^- \quad (6)
\]
\[
4\text{Fe}^{2+}(aq) + 10\text{H}_2\text{O}(l) + \text{O}_2(g) \rightarrow 4\text{Fe(OH)}_3(s) + 8\text{H}^+(aq) \quad (7)
\]
Cathode:
\[
8\text{H}^+(aq) + 8\text{e}^- \rightarrow 4\text{H}_2(g) \quad (8)
\]
Overall:
Mechanism 2

Anode:
\[ \text{Fe (s)} \rightarrow \text{Fe}^{2+} \text{(aq)} + 8e^- \]  \hspace{1cm} (10)
\[ \text{Fe}^{2+} \text{(aq)} + 2\text{OH}^- \text{(aq)} \rightarrow \text{Fe(OH)}_2 \text{(s)} \]  \hspace{1cm} (11)

Cathode:
\[ 2\text{H}_2\text{O(l)} + 2e^- \rightarrow \text{H}_2\text{(g)} + 2\text{OH}^- \text{(aq)} \]  \hspace{1cm} (12)

Overall:
\[ \text{Fe (s)} + 2\text{H}_2\text{O(l)} \rightarrow 4\text{Fe(OH)}_3 \text{(s)} + 4\text{H}_2\text{(g)} \]  \hspace{1cm} (13)

The effect of electrical potential

The electrical potential effect on colour removal

The colour reduction increased with electrical potential as shown in Figure 2. This may be explained by the release of metal ions increasing with electrical potential. Therefore, there is an increase in floc production and hence an improvement in the colour removal efficiency. According to Kashefialasl [17], when current density was increased from 32 to 127.8 A/m² for 6 minutes, the effectiveness would increase from 21% to 83.5% from the initial dye concentration at 50 mg/l. Carneuro, et al. [9], used the electrocoagulation process to reduce reactive dye (Blue 4 Dye). They reported that the effectiveness in colour removal and organic matter removal were 50% and 64% respectively. Daneshava, et al, [18], reported that the conditions for basic dye removal of 60-80 A/m² and 5 minutes electrolysis time could reduce basic dye (C.I. Basic Red 46 and C.I. Basic Blue 3) effectively.

The electrical potential effect on pH

Electrical potential effected the pH of water significantly. As shown in Figure 3, the pH value increased as the electrical potential of electrocoagulation process was increased.

Figure 3. Effect of electrical potential on the pH of solution.
From these results, it was seen that because of the electron transfer at the cathode electrode when transmitting the electrical current, hydrogen cation and water molecules would receive electrons which caused hydrogen gas and hydroxide ions as shown below:

\[
\begin{align*}
\text{H}^+_{(aq)} + 2e^- & \rightarrow \text{H}_2(g) \quad (14) \\
2\text{H}_2\text{O}(l) + 2e^- & \rightarrow \text{H}_2(g) + 2\text{OH}^-_{(aq)} \quad (15)
\end{align*}
\]

From the equation above, when the water molecule received electrons, hydroxide ions would be formed, which in turn increased pH.

**The electrical potential effect on dissolved solids**

The effect of electrical potential on dissolved solid removal was investigated by varying electrical potential with 180 minutes. The result is shown in Figure 4.

![Graph showing dissolved solid removal vs. electrical potential for reactive dye and basic dye](image)

**Figure 4. Effect of electrical potential on the efficiency of dissolved solid removal.**

Figure 4 depicts the dissolved solid removal efficiency as a function of electrical potential. Electrical potential effected the efficiency of dissolved solid removal significantly. The dissolved solid removal efficiencies increased as the electrical potential was increased. The aluminium electrode at 20 volts and 180 minutes of electrolysis time, could dispose of 35.18% dissolved solids from reactive wastewater, whereas the electrolysis cell with iron electrode at 25 volts and 180 minutes of electrolysis time could dispose of 13.42% dissolved solids from basic dye wastewater.

**Effect of electrolysis time**

The effect of electrolysis time was studied at constant electrical potential. The electrolysis time effected colour removal significantly. Figure 5 illustrates the removal of colour as a function of electrolysis time.
It can be seen from Figure 5 that the electrolysis time effected colour removal significantly. The colour removal efficiencies increased as the electrolysis time was increased. When electrolysis time increased to a specific level, the effectiveness tended to decrease. According to Chen, et al, [10], the electrolysis time decreased from 60 to 6.5 minutes when density electrolytic current was increased from 12.5 A/m² to 108.9 A/m².

Effect of electrode area

The electrode area effected colour removal, pH, dissolved solids removal and turbidity removal significantly as shown in Table 1.

### Table 1. T test of the mean of colour removal, pH change, dissolved solids removal and turbidity removal at 25 volts, 120 minutes electrolysis time and different electrode area.

<table>
<thead>
<tr>
<th>Size</th>
<th>N</th>
<th>Colour Removal (%)</th>
<th>pH Change (%)</th>
<th>DS Removal (%)</th>
<th>Turbidity Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>SD.</td>
<td>t</td>
<td>Mean</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>69.92</td>
<td>1.62</td>
<td>11.57</td>
<td>11.74</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>19.69</td>
<td>7.34</td>
<td>-3.75</td>
<td>7.61*</td>
</tr>
</tbody>
</table>

* significant (P<0.05)

`size 1 is 3x12.5x0.6 cm and size 2 is 6x12.5x0.6 cm.`

From the results presented in Table 1, it was found that the greater the electrode area, the less effective was the water treatment. This was due to the increase of electrode area causing a corresponding increase of coagulants. The entire effectiveness of the coagulation process depended on the appropriate amount of coagulant [19]. If there was too much or too little coagulant, it would render the coagulation process ineffective. Therefore, if the electrode area was increased, electrical potential and electrolysis time would be decreased.

### Process comparison

For comparative purposes, the efficiency of the current wastewater treatment system employed by a local textile dyeing company, Charoenchai Industry was examined. This system involves treatment by aerated lagoon, followed by chemical oxidation process. The efficiency of both wastewater treatment processes were compared as shown in Table 2.
Table 2. Efficiency of wastewater treatment comparing different methods.

<table>
<thead>
<tr>
<th>Type of Treatment</th>
<th>pH Before treatment</th>
<th>pH After treatment</th>
<th>Colour Removal</th>
<th>DS Removal</th>
<th>SS Removal</th>
<th>Turbidity Removal</th>
<th>COD Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.70</td>
<td>9.22</td>
<td>85.61</td>
<td>30.67</td>
<td>66.67</td>
<td>20.61</td>
<td>79.51</td>
</tr>
<tr>
<td>2</td>
<td>6.70</td>
<td>7.97</td>
<td>69.39</td>
<td>-20.45</td>
<td>61.27</td>
<td>20.08</td>
<td>77.88</td>
</tr>
</tbody>
</table>

1; treatment by electrocoagulation process  2; treatment by aeration lagoon.

From Table 2, the quality of the basic dye wastewater treated by the electrocoagulation process was significantly better than that normally treated by factories using aerated lagoon and oxidation process in most of the parameters except pH solution.

**Potential for reusing water from the electrocoagulation process**

By comparing the quality of the water normally used in the operating process and reused water from the electrocoagulation process, the quality of basic dye wastewater treated by the electrocoagulation method was no better than the water normally used in the operating process in most of the parameters except for water hardness, as shown in Table 3.

Table 3. T test of the mean of water quality between water normally used in the operating process and reused water from electrocoagulation process.

<table>
<thead>
<tr>
<th>Water quality</th>
<th>Type of water</th>
<th>mean</th>
<th>SD</th>
<th>t</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour</td>
<td>water normally used in the operating process</td>
<td>0.004</td>
<td>0.001</td>
<td>-5.715*</td>
</tr>
<tr>
<td></td>
<td>Reused water</td>
<td>0.042</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>water normally used in the operating process</td>
<td>7.63</td>
<td>0.28</td>
<td>-5.657*</td>
</tr>
<tr>
<td></td>
<td>Reused water</td>
<td>9.22</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>conductivity</td>
<td>water normally used in the operating process</td>
<td>452.00</td>
<td>6.93</td>
<td>-5.042*</td>
</tr>
<tr>
<td></td>
<td>Reused water</td>
<td>544.67</td>
<td>31.07</td>
<td></td>
</tr>
<tr>
<td>turbidity</td>
<td>water normally used in the operating process</td>
<td>0.29</td>
<td>0.06</td>
<td>-118.453*</td>
</tr>
<tr>
<td></td>
<td>Reused water</td>
<td>5.30</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>suspended solids</td>
<td>water normally used in the operating process</td>
<td>0.03</td>
<td>0.02</td>
<td>-13.653*</td>
</tr>
<tr>
<td></td>
<td>Reused water</td>
<td>0.68</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>water hardness</td>
<td>water normally used in the operating process</td>
<td>82.48</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Reused water</td>
<td>82.48</td>
<td>2.00</td>
<td></td>
</tr>
</tbody>
</table>

*0.05 significant (P<0.05)

These results demonstrated that it was possible to reuse the water but it must first be passed through a filtration process to remove suspended solids and reduce turbidity. However, some caution should be taken to determine the amount of heavy metals in the water, as these will have a detrimental effect on textile quality.

**Conclusion**

Electrocoagulation is one of the most effective techniques to remove colour and organic pollutants from wastewater. The decolourization of dye solution by this electrochemical process was affected by electrode material, electrical potential and electrolysis time. The results showed that the electrical potential was the most effective parameter. The proper conditions for reactive wastewater treatment by coagulation process were 20 volts aluminium electrode at 180 s. electrolysis time. The effectiveness in colour removal and dissolved solids were 96.05% and 35.18%, respectively. The proper conditions for basic wastewater treatment by coagulation process were 25 volts iron electrode at 180 s. electrolysis time. The effectiveness in colour removal, dissolved solids, suspended solids, turbidity and COD were 85.61%, 30.67%, 66.67%, 20.61%, and 79.51% respectively. It is recommended that further work should be undertaken to study the lifetime of electrodes, space between electrodes and a
comparison of the cost effectiveness of water treatment by coagulation with chemicals and with electrical current.

Acknowledgements
The authors would like to thank Rajamangala University of Technology Krungthep for financial support and Charoenchaikarnyom for supplying the wastewater. The authors are also grateful to the anonymous reviewers for their valuable comments and suggestions.

References


