Decolorization of High Polluted Textile Wastewater by Indirect Electrochemical Oxidation Process

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ABSTRACT

The present study attempts to treat a synthetic textile effluent containing indigo dye by indirect electro-oxidation. Electrochemical degradation process was performed using Graphite as anode and Stainless Steel as cathode. The influence of effluent pH, supporting electrolyte concentration and the current intensity on pollutant degradation was studied. The best removal of organic compounds contained in the waste has been obtained at pH 13, low electrolyte concentration and current intensity (0.1M and 200 mA, respectively). COD and percentage colour removal were 75% and 43% respectively. Due to its effectiveness and ease in operation, this technique can be applied for treatment of a large volume and industrial scale of textile wastewater.

Keywords: electro-oxidation; dye treatment; indigo; colour removal; COD reduction

INTRODUCTION

Dyes pollutants from the textile industry are an important source of environment contamination. They pose serious problems because of their strong colour, high COD and low biodegradability (Shen et al., 2006). These effluents usually contain dyes such as indigo, a well known non biodegradable dye, which causes environmental concern (Dogan, Türkdemir, 2005; Ahmadi et al., 2005). Therefore, most of traditional methods of wastewater treatment are becoming inadequate. Electrochemical technology and its application on wastewater treatment have become increasingly interesting, because of its advantage especially for colour removal (Vlyssides et al., 2000; Shen et al., 2006). Consequently, it is imperative to study these factors and to find how to operate electrochemical oxidation more effectively.

In the present study, therefore, we report the investigation of the decolourization and the mineralization of aqueous solutions of textile dye indigo by indirect electrochemical oxidation and the effects of experimental parameters on colour removal and chemical oxygen demand reduction.

ELECTROCHEMICAL PROCESS

Pollutants can be destroyed electrochemically by conducting a direct...
anodic oxidation or an indirect oxidation process. The schema of these two processes is illustrated in Figure 1. In a direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction (Li-Choung Chian et al., 1995). The direct electro-oxidation rate of organic pollutant is dependent on the catalytic activity of the anode, diffusion rate of organic compounds in the active points of the anode and the applied current intensity. Indirect electro-oxidation of pollutants, which was observed to be most efficient method on decolourisation and mineralisation, can be conducted when chloride, ferric or silver are present. The first being the most important from the point of view of practical application, as chlorides are a common constituent of several industrial textile wastewaters. The indirect electro-oxidation rate is dependent on the diffusion rate of strong oxidants electro-formed into solution which are able to completely convert all organics into water and carbon dioxide.

![Direct Oxidation Mechanism](image)

**FIGURE 1: The scheme of pollutant removal pathway in electrochemical oxidation process**

**Experimental**

**Chemicals:**

The following characteristics of indigo dye are presented in Table 1. Sodium chloride was used as supporting electrolyte (CHEMI-PHARMA). Indigo (BASF), sulphuric acid (PROLABO), sodium hydroxide (PANREAC ACS-ISO) and all other chemicals used were analytical grade. Dispersing agent (Dispertagol SMS; BEZEMA) and wetting agent (Subitol LSN; BEZEMA) were of technical grade.

**TABLE 1: Main characteristics of Indigo**

<table>
<thead>
<tr>
<th>Name</th>
<th>Vat blue 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour Index</td>
<td>CI.73000</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Amax</td>
<td>681.5 nm</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>262 g/mol</td>
</tr>
</tbody>
</table>

The characteristics of the textile wastewater are showed in Table 2.

**TABLE 2: Characteristics of textile wastewater**

<table>
<thead>
<tr>
<th>Character</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13</td>
</tr>
<tr>
<td>[Indigo]</td>
<td>$7.5 \times 10^{-3}$ (g/L)</td>
</tr>
<tr>
<td>Absorbance (at 681.5 nm)</td>
<td>1.58</td>
</tr>
<tr>
<td>COD</td>
<td>17540 (mg/L)</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>150 (mg/L)</td>
</tr>
</tbody>
</table>

**Electrolytic apparatus:**

The electrochemical cell (Figure 2) consists of an undivided reactor with two parallel electrodes having an inter-electrode gap of 10 mm. The electrochemical cell has a volume of 100 mL. All electrolyses were performed in intensiostatic mode using graphite anode (a geometric surface area of about 35 cm$^2$) and stainless steel cathode (geometric surface area of about 15 cm$^2$). Both the anode and cathode were placed vertically and parallel to each other in the electrolyte cell. The electric power required during the electrolysis experiments was provided by a laboratory DC Power Supply (G ZIMMERMAN AG LUZERN Generator). The electrolytic cell was equipped with a magnetic stirrer in order to keep the electrolyte well mixed.
Procedure:

Firstly, the pH of solution was fixed at the desired value by adding sulphuric acid. After mixing the solution, the operating parameters (chloride concentration and current intensity) were varied to study their influences. Experimental results from these experiments were compared in order to determine the optimal operational conditions for the treatment of such synthetic wastewater. All electrolyses were done at room temperature.

Methods of analysis:

Absorbance measurements were carried out with a UV-Visible spectrophotometer (Shimadzu UV-256) recording the spectra over the 190-900 nm range. To estimate colour removal, the disappearance of the absorbance peaks of the solution was monitored. Colour removal ratio was calculated as follows:

\[
ABS(\%) = \frac{ABS_{(681)t} - ABS_{(681)i}}{ABS_{(681)i}} \times 100 \tag{1}
\]

Where ABS (681), is the average value of absorbency at 681 nm. ABS (681), is the value obtained at time t.

Chemical Oxygen Demand tests were performed according to Standard Methods of Examination of Water and Wastewater (APHA, 1995). The percentage of dye mineralization was evaluated from the measurement of COD removal.

\[
COD(\%) = \frac{COD_i - COD_t}{COD_i} \times 100 \tag{2}
\]

Where COD, corresponds to the initial value and COD, is the value obtained at time t.

RESULTS AND DISCUSSION

Preliminary study:

During the preliminary investigations different anode and cathode materials such as platinum, carbon, iron and aluminium and tow cell types (divided and undivided) were tested. The undivided cell and the graphite/stainless steel were selected as the working cell and anode/cathode respectively according to the results of the pre-investigation. The results showed also that colour removal occurred only in the presence of NaCl. Electrolysis duration was also fixed at 120 min.

Determination of optimum pH value:

To examine the effect of pH on the decolourisation process, the dyeing solution was adjusted initially to the desired pH for each experiment, using concentrated sulphuric acid after the addition of NaCl (0.1M, 0.5M and 1M). The experiments have been carried out at 2.0, 7.0 and original pH (=13). As shown in the Figure 3, the pH change affects the nature of chlorine forms (Deborde, von Gunten, 2008).

![FIGURE 3: Relative distribution of main aqueous chlorine species as a function of pH at 25 °C and for a chloride concentration of 5x10^{-3} M (177.5mgL^{-1}).](image)
The effect of pH on electrochemical degradation of Indigo was illustrated in Figure 4. The experiments were carried out with 0.1M chloride concentration. The results of electrolysis done on pH 2, 7 and 13 were compared in terms of colour and COD removal. From Figure 4, it is evident that the effect of pH value on the degradation of dyes is remarkable under highly basic conditions. This result can be explained by the basic structure of indigo and ClO\(^{-}\) ions, which act as better oxidizing agents in basic media. Therefore, pH 13 was selected as the operating pH value.

Using sodium chloride as the supporting electrolyte at pH 13, colour removal and dye mineralization percentage were plotted against NaCl concentration to determine the operating value. The effect of changing the electrolyte concentration (0.1M, 0.5M and 1M) on colour and COD removal are illustrated in Figure 5 and 6. From these figures, it is clear that indigo dye is quite a recalcitrant substance. Experiments showed that in the electrolysis of indigo with chloride, an indirect electrochemical oxidation effect of chlorine/hypochlorite is the main pathway for removal of pollutants. The superior effect of chloride may be due to the indirect oxidation effect of chlorine and the “in situ” generation of hypochlorite ions which seems to be the most effective oxidation specie to the fragmentation of indigo molecule. Although the results indicate that the colour removal increases with increasing the chloride concentration in acidic and neutral medium (pH 2 and 7 respectively), a different behaviour was noted in the case of pH 13. High concentration of the electrolyte support causes a decrease in the colour removal. An electrolyte concentration of 0.1M was selected as the operating concentration owing to the known toxic effects of chloride excess. Electrolyte concentration higher than 0.5M does not have a major effect on the colour removal nor on the COD removal.

**Optimisation of NaCl concentration:**

The general chloride reactions involved in electrochemical oxidation are presented as follow:

- **Anode:** \(2Cl^- \rightarrow Cl_2 + 2e^-\)
- **Cathode:** \(2e^- + 2H_2O \rightarrow 2OH^- + H_2\)
- **Overall:** \(2OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O\)

Chlorine (Cl\(_2\)), hypochlorous acid (HClO) and hypochlorite ions (ClO\(^{-}\)) are strong oxidizing species and are often referred to as “active chlorine” (Deborde, Gunten, 2008).

Colour removal is of prime importance for textile industries. It is clear from Figure 5 that the electrochemical
oxidation process has effectively reduced the colour of the indigo solution. At pH 13, the indirect oxidation effect of chlorine/hypochlorite is the predominant mechanism for decolourisation (Szpyrkowics et al., 2000; Deborde, Gunten, 2008).

For high concentration of sodium chloride, the low percentage of COD removal is probably caused by the production of chloramines. These compounds are very toxic and enhance the COD of the wastewater.

The purpose of the study was to decolourize the solution of indigo dye and to reduce the COD value of the solution as much as possible. The best compromise between colour and COD removal was obtained at 0.1M chloride concentration.

**Determination of optimum current intensity value:**

The effect of varying the electrolyse current at constant electrolyte concentration (0.1M) and pH 13 is shown on Fig 6.

As current intensity increases, the pollutant degradation rate increases initially. However, once the current intensity reaches a certain value (200 mA), referred as limiting current intensity, the degradation rate does not increase any more and is determined by the mass transfer rate. The increased current beyond the limiting current intensity is not for oxidizing pollutants but for producing O2, resulting in a decrease in current efficiency.

**UV–VIS spectrophotometric investigations in optimal conditions:**

The changes in absorbance characteristics of indigo dyeing solution were investigated over a large wavelength interval during the electrochemical decolourization process. The absorbance spectral changes every 15 min of indigo effluent are shown in Figure 8. The spectra show that there is a maximum absorbance at 681.5 nm in the visible region. This peak disappears gradually during the electrochemical oxidation process. After 120 min of electrolysis, the absorbance peaks at 681.5 nm have been notably reduced. The decreasing of the visible band is due to the fragmentation of the organic molecule of indigo. After 45 min of electrolyse, the absorbance decreases rather slowly. It can be concluded that the conjugated bands of dye must be destroyed and the molecules are broken into small ones probably more difficult to degrade.
CONCLUSIONS

Indirect electrochemical oxidation of a synthetic wastewater containing Indigo dye was investigated using Graphite anode and Stainless Steel cathode in the presence of chloride. The process involves the liberation of chlorine at the anode and hydroxide ion at the cathode, resulting in the in situ generation of hypochlorite ion, which is a powerful oxidant. Methods of changing electrolyte concentration, initial pH, and applied intensity to improve degradation effect were studied. COD and percentage colour removal were 43% and 75% respectively at pH 13, 200 mA and 0.1 M chloride concentration. The electrolyte concentration was maintained as low as possible to avoid excess chloride pollution. The overall experimental results indicate that this electrochemical method can be used effectively as a pre-treatment stage prior to conventional treatment.

REFERENCES


