Treatment and Decolourisation of an Azo Dye in Industrial Effluent

Rajeev Jain*, Meenakshi Bhargava and Nidhi Sharma

Department of Environmental Chemistry, Jiwaji University, Gwalior, 474 011

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The electrochemical behaviour of Orange II is studied voltammetrically using Pt foil and steel foil as working electrodes, while Pt wire and Ag/AgCl were used as auxiliary and reference electrodes respectively. Controlled potential electrolysis was carried out at -1.20 V. The decrease in cathodic peak and peak current lead to decolourisation of solution (2 x 10^-4 m) with a significant decrease in COD from 1840 mg/L to 174 mg/L. Orange II is found to yield a mixture of sulphanilic acid and 1-amino-2-naphthol upon electrochemical reduction. Based on voltammetric and spectrophotometric analysis, rate of the reaction was determined and found to be of first order.

Keywords: Decolourisation, Azo dye, Industrial effluent

Introduction

Most of the industries use dyes and pigments to colour their products. The largest consumers of these dyes are textile, tannery, paper and pulp, pharmaceuticals, cosmetics, food processing units and they are, in turn, the most serious polluters of our environment. The textile industry in India is one of the oldest and largest in the country. These mills require volumes of water of high purity and generate equally large volumes of wastewater, which is highly coloured, and complex. Colour removal from these effluents has been getting more attention in the last few years, not only because of its toxicity but also due to its visibility. Recent estimates indicate that, approximately 12 per cent of synthetic dyes used every year are lost during manufacture and processing operations and 20 per cent of these lost dyes enter the environment through effluents that result from the treatment of residual industrial waters. The proper treatment of aqueous wastes is fundamental for the preservation of environmental equilibria and the quality of aquatic systems. Electrochemical methods for pollution abatement have been shown to be viable alternative or complements to other treatment methods, in some cases, especially when pollutants are recalcitrant to biological processing, electrochemical methods are found to be useful precursors to biological treatment. In principle, any pollutant capable of undergoing oxidation or reduction in given experimental conditions at an electrode can be transformed and/or removed from wastewater at appropriate potentials.

The present work reports the results of electrochemical studies on an azo dye Orange II, in particular reference to colour removal and wastewater treatment. It is an acid dye and the acidic group acts as auxochrome in these dyes. They are used to dye wool, silk, nylon, and polyacrylic fibres.

Experimental

Instrumentation

Controlled potential electrolysis (CPE) was carried on BAS CV27 Cyclic Voltamograph in connection with a Digital Electronic 2000 Omnigraph X-Y/t recorder. A three-electrode cell was used for the purpose. The cell comprises a glass container with a cap having holes for introducing electrodes and nitrogen gas. The working electrode is Pt foil (3 x 3 cm^2), reference is Ag/AgCl and auxiliary electrode, a Pt wire which was directly poured in the solution. Cyclic voltammograms were taken using EG&G Princeton Applied Research VersaStat-II Potentiostat.

* Author for correspondence
E-mail: gwlsosmica@sancharnet.in
The pH metric measurements were made on Hach EC 40 Bench top digital pH meter fitted with a glass electrode and saturated calomel electrode as reference, which was previously standardized with buffers of known pH in acidic and alkaline medium. The electrolysed solution was subjected to TLC for end product analysis. TLC was done on ready-made plates of E-Merck (silica gel 60 F254) with overall dimensions of 20 x 20 cm. For end product identification, TLC was also employed using Dioxane : Water (10 : 2) as mobile phase. The initial compound could be seen with the naked eye, while for the electrolysed solution the plate was viewed under UV lamp. The reaction kinetics was studied with the help of UV-visible spectrophotometer (Elanco SL-159). The rate of decrease of colour with time was continuously monitored. For measuring pollutional load of electrolysed solution, Chemical Oxygen Demand (COD) of both coloured and decolourised/ electrolysed solutions were recorded. COD Digestion Apparatus (Spectra lab-2015-S) was used for carrying out the experiment.

Reagents and Solutions

Orange II of Standard Fluka Chemika was used. 2 x 10^{-3} M stock solution of Orange II in 50 mL of distilled water was prepared. 1.0 M KCl was prepared in distilled water as a supporting electrolyte. Britton-Robinson buffers in the pH range 2.5-12.0 were prepared in distilled water by adding suitable amounts of 0.4 M NaOH solution (basic solution) to a stock solution composed of a mixture of phosphoric acid, boric acid, and glacial acetic acid (acidic solution). Solution was stirred and left overnight to attain equilibrium. All the chemicals used were of AR grade.

For COD determination, potassium dichromate (0.25 N) and ferrous ammonium sulphate (0.1 N), were prepared in distilled water. Distilled water was used for the necessary dilutions.

Procedure

For cyclic voltammetry (CV) and controlled potential electrolysis (CPE) the solution was prepared by taking 9.0 mL of the stock solution and 1.0 mL of 1.0 M KCl (as supporting electrolyte). 1.0 mL of stock solution was diluted to 10.0 mL with BR buffer solutions. The solution was deaerated by passing nitrogen gas for about 15 min and, thereafter, a blanket of nitrogen gas was maintained throughout the experiment. The cyclic voltammograms were recorded in the beginning of the experiment and then the solution was subjected to electrolysis at a controlled potential of -1.20 V. Further, at the end of electrolysis, i.e., when the solution became colourless and current was significantly decreased, the voltammograms were again recorded.

For coulometric determination of number of electrons 'n' consumed in the reduction, solution was prepared in the similar fashion as for cyclic voltammetric studies. With the progress of the electrolysis the colour of the solution gradually got faded and finally a colourless solution was obtained. The current decreases exponentially with time and becomes practically zero after some time. Value of Q was read directly from the instrument and by the application of \( Q = nFN \), the value of 'n' could be calculated.

During controlled potential electrolysis the absorbance and current values were recorded at regular intervals with respect to time. An aliquot of the solution under study was taken out in the quartz cuvette and was put in the UV-Vis spectrophotometer with distilled water as reference. The decrease in absorbance value with passage of time was noted.

Results and Discussion

Effluents, which contain azo reactive dyes, are very difficult to treat in environmental systems, due to the sulphonate acid groups, which makes the dyes very water-soluble and polar\(^ {12-14} \). Therefore, such dyes are not readily adsorbed onto the non-polar carbon surface. The dye must first be degraded and its degradation products adsorbed. The reduction cleaves the azo linkage of the dye, producing the corresponding aromatic amines and resulting in decolourisation. Direct photolysis has not been found to be effective in the degradation of azo dyes. Biological degradation is slow for many azo dyes and does not proceed at all for Orange II. Recent studies have shown that oxidation of organic compounds by way of Fenton's reagent are useful in the degradation of this type of compounds\(^ {15,17} \). This low BOD 5: COD ratio values (less than 0.1) indicate their resistance to conventional biological treatment\(^ {18} \). Electrochemical reduction is a superior technology for physical treatment of dyes, as there is no simultaneous addition of anions, such as sulphate or
chloride. The main reagent used is the electron, which is a clean reagent, and usually there is no need for adding extra chemicals.

**Cyclic Voltammetry**

The comparative voltammograms are shown in Figure 1. The electrochemical characteristics are given in Table 1. Orange II gives a 4-electron, irreversible, diffusion controlled cathodic peak.

In aqueous medium, a peak current (ip, c) of -16.21 μA was observed at a scan rate 150 mV/s, which decreases to -9.0 μA in electrolysed solution. On reversing the scan, an anodic peak involving one electron was observed. There was increase in anodic peak current from 18.27 μA to 57.31 μA. Irreversible nature of the electrode process was indicated by a negative shift in peak potential values with increasing scan rate (50-200 mV/s), as shown in Figure 2. Reduction was found to be diffusion controlled, as evident by the straight-line plot of ip, c vs v^1/2 (scan rate) (Figure 3). A positive shift in anodic peak potential with increasing scan rate was also observed. There was also an increase in both ip,c and ip,a (i.e. peak currents) with increase in scan rate. Same trend

![Cyclic voltammograms of Orange II (2.0 × 10⁻⁴ M in distilled water) at Pt working electrode, scan rate 200 mV/s. (i) Before electrochemical treatment and (ii) After electrochemical treatment](image)

**Table 1— Electrochemical characteristics of Orange II in aqueous medium at various scan rates at Pt foil working electrode, conc. = 2 × 10⁻³ M**

<table>
<thead>
<tr>
<th>Working electrode</th>
<th>Scan rate (mV/s)</th>
<th>v^1/2</th>
<th>ip, c (μA)</th>
<th>Ep, c (V)</th>
<th>ip, a (μA)</th>
<th>Ep, a (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum Foil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.07</td>
<td>-6.43</td>
<td>-0.402</td>
<td>15.16</td>
<td>0.758</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td></td>
<td>-4.23</td>
<td>-0.402</td>
<td>17.36</td>
<td>0.794</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>10.0</td>
<td>-13.61</td>
<td>-0.402</td>
<td>16.97</td>
<td>0.737</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td></td>
<td>-11.00</td>
<td>-0.402</td>
<td>53.40</td>
<td>0.804</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>15.0</td>
<td>-18.21</td>
<td>-0.399</td>
<td>18.27</td>
<td>0.719</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td></td>
<td>-9.00</td>
<td>-0.399</td>
<td>57.31</td>
<td>0.801</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>200</td>
<td>-18.81</td>
<td>-0.431</td>
<td>19.57</td>
<td>0.708</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td></td>
<td>-10.35</td>
<td>-0.420</td>
<td>57.31</td>
<td>0.790</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A = Before electrochemical treatment, B = After electrochemical treatment
was observed in both acidic and alkaline pH (3.8 and 8.8, respectively).

**Electrochemical Behaviour at Varying pH**

A negative shift is observed in the anodic peak with increase in pH from 2.5 to 12.0, while the cathodic peak shows a positive shift with increase in pH. A significant cathodic current and peak in highly alkaline or acidic medium was observed, while in between 5.0-8.8 pH, no significant cathodic peak was observed. In this pH range the \( E_{p,a} \) (anodic peak potential) shows a negative shift even in electrolysed solution. In highly acidic pH (2.5, 3.8) and in highly alkaline pH (10.5, 12.0) there is a positive shift in the \( E_{p,a} \) values in electrolysed solution. In the entire pH range, there is significant decrease in both anodic and cathodic peak current values, as reported in Table 2.

Effect of concentration of azo dye on redox process was examined and it was observed that with increase in concentration of the azo dye, peak

![Figure 2 - Cyclic voltammograms of Orange II (2 x 10^-4 M in distilled water) at Pt working electrode at varying scan rates; (i) 50, (ii) 100, (iii) 150, (iv) 200 mV/s](image)

**Table 2 - Electrochemical characteristics for Orange II at different pH at scan rate = 100 mV/s, conc = 2 x 10^-4 M**

<table>
<thead>
<tr>
<th>pH</th>
<th>( i_{p,c} ) (( \mu )A)</th>
<th>( E_{p,c} ) (V)</th>
<th>( i_{p,a} ) (( \mu )A)</th>
<th>( E_{p,a} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>(i) -20.26</td>
<td>(i) -0.350</td>
<td>(i) 59.88</td>
<td>(i) -0.518</td>
</tr>
<tr>
<td></td>
<td>(ii) —</td>
<td>(ii) 260.20</td>
<td>(ii) 95.00</td>
<td>(ii) -0.695</td>
</tr>
<tr>
<td>3.8</td>
<td>(i) -105.00</td>
<td>(i) -0.694</td>
<td>(i) 35.47</td>
<td>(i) -0.537</td>
</tr>
<tr>
<td></td>
<td>(ii) -95.00</td>
<td>(ii) -0.694</td>
<td>(ii) 55.00</td>
<td>(ii) -0.410</td>
</tr>
<tr>
<td>5.0</td>
<td>(i) -148.70</td>
<td>(i) -0.797</td>
<td>(i) 120.90</td>
<td>(i) -0.484</td>
</tr>
<tr>
<td></td>
<td>(ii) —</td>
<td>(ii) —</td>
<td>(ii) 100.00</td>
<td>(ii) -0.550</td>
</tr>
<tr>
<td>6.0</td>
<td>(i) -86.51</td>
<td>(i) -0.726</td>
<td>(i) 83.06</td>
<td>(i) -0.705</td>
</tr>
<tr>
<td></td>
<td>(ii) —</td>
<td>(ii) —</td>
<td>(ii) 60.00</td>
<td>(ii) -0.709</td>
</tr>
<tr>
<td>10.5</td>
<td>(i) -23.10</td>
<td>(i) -0.384</td>
<td>(i) —</td>
<td>(i) —</td>
</tr>
<tr>
<td></td>
<td>(ii) -18.19</td>
<td>(ii) -0.271</td>
<td>(ii) 74.52</td>
<td>(ii) -0.833</td>
</tr>
<tr>
<td>12.0</td>
<td>(i) -24.31</td>
<td>(i) -0.338</td>
<td>(i) 145.30</td>
<td>(i) -0.847</td>
</tr>
</tbody>
</table>

A = Before electrochemical treatment, B = After electrochemical treatment
potential shifts towards more negative potential, indicating the difficult reduction and oxidation with concentration. The time taken for decolourisation also decreases significantly with decrease in concentration, as shown in Table 3. Decrease in ip,c (cathodic peak current) with time was observed for Orange II, as reported in Table 4.

Controlled Potential Electrolysis and Coulometry

Controlled potential electrolysis of $2 \times 10^{-4} \, M$ solution of Orange II dye solution was carried out at electrolysis potential of $-1.20 \, V$. With Pt foil as working electrode the reaction took approximately 8 h for complete decolourisation and reduction of cathodic peak current.

Coulometric measurements were carried out to calculate the number of electrons involved in the overall electrode process and it was found to be $4 \pm 0.2$. Normally, at all pH values azo group is reduced in two-electron electrode reaction to hydrazobenzene but because of the presence of strong electron releasing substituent -OH the hydrazo derivative is unstable and single four-electron wave may result. It was also found that if reduction was continued for a sufficiently long time, a final 'n' value of four was always obtained for -OH substituted compounds. Electrolysis time for complete removal of colour was extended up to 10 h at a concentration of $20 \times 10^{-4} \, M$.

Spectral Studies

The kinetics of the decomposition was also monitored by recording changes in absorbance with time at $\lambda_{\text{max}} \, 483 \, \text{nm}$. The rate of decrease of absorbance with time was noted by plotting graph between absorbance and time and log absorbance vs time. For kinetic studies the solution (being intensely coloured) was further diluted to $2 \times 10^{-5} \, M$. The reactions obeyed first order rate expression with rate constant $1.15 \times 10^{-1} \, \text{min}^{-1}$ and $R_{\text{obs}}/\min ^{-1} \, 2.3 \times 10^{-6}$.

Chromatographic Studies

End products of controlled potential electrolysis were separated by TLC in Dioxane:Water (10:2) solvent system. TLC showed the formation of only one product, indicating that azo grouping is being reduced to colourless hydrazo compound.

Chemical Oxygen Demand (COD)

COD of initial coloured and electrolysed solutions was carried out and it was observed that the COD values show a significant decrease from 1840 mg/L to 174 mg/L, indicating less toxicity of the electrolysis products thus formed.

Redox Mechanism

As evident from the above studies, it can be inferred that electrochemical reduction of Orange II takes place in two well-defined 2-electron reduction step, involving cleavage of chromophoric azo group. Cyclic voltammograms of completely reduced
solution show absence of any reduction peak, which indicates absence of any electroactive species. The single product formation, as evident by TLC, and four-electron irreversible peak clearly indicates the reduction of $-\text{N} = \text{N}-$ to $\text{NH} \cdot \text{H}^+$ groups and decolourisation due to reduction of chromophoric azo group. Based on the results of cyclic voltammetry, coulometric, chromatographic and spectral studies, following electrode reduction mechanisms, as given in Scheme I for Orange II may be proposed at Pt foil working electrode. The proposed mechanism is supported by other reported studies.

Acknowledgement

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References


