EFFECT OF SUPPORTING ELECTROLYTE AND SUBSTITUENTS ON THE ELECTROCHEMICAL TREATMENT OF MONOAZO BENZENE DYES

I. Alamddine, M.M. El Jamal

Chemistry Department, Faculty of Sciences
Lebanese University, El Hadath, Lebanon
E-mail: mjamal@ul.edu.lb.

Received 23 March 2009
Accepted 30 April 2009

ABSTRACT

Toxic azo dyes have been widely used in industries and are then present in wastewater. Thus the treatment of polluted water becomes a great necessity. In this work the electrochemical degradation of monoazo benzene derivatives (Methyl Red (MR), Methyl Orange (MO) and Methyl Yellow (MY)) was investigated in order to understand better the factors affecting the electrodegradation. The effect of several experimental parameters: pH, current, nature of the supporting electrolyte and substituents at the aromatic ring on the degradation rate were investigated. The decomposition rate increases with the decrease of pH and the temperature. Also it increases with respect to the azo dye in the following order: MY, MR, MO and with respect to the supporting electrolyte in the following order: Na₂SO₄ ~ NaF, KI, KCl, KBr.

Keywords: monoazo benzene dyes, electrochemical degradation, effect of supporting electrolyte, effect of substituents.

INTRODUCTION

The textile and carpet industries are one of the most polluting industries generating large volumes of wastewater during cloth dyeing and washing processes. Various chemicals such as wetting agents, dyes, surfactants, fixing agents and other additives are used in wet processes (bleaching, dyeing) and as a result large volumes of highly polluted wastewater are produced [1-3]. Azo dyes (compounds contains at least one –N=N-) are the most widely used colorants (accounting for up to 70 % of the overall colorant production) due to their bright colours, excellent colourfastness, and ease of application [4-6]. It has been estimated that more than 700,000 tons of the dyes are used of which over 15-20 % are left in the effluent during the dyeing process [7].

Effluents released from textile and carpet industries contain highly refractory and often toxic compounds with strong colour. When colorants are released in receiving water bodies, they interfere with bacterial growth due to the absorption of sunlight. Minor releases of colorants impact health disorders to organisms exposed to them [8]. The removal of hazardous dyes from industry effluent is very important for the environment [9].

Developing a treatment technology that can provide complete degradation of wastewater without generating toxic sludge has been a priority task for textile industries around the world. Several methods are used: physical (adsorption) [10], aerobic and anaerobic biological processes [11-13], chemical oxidation (ozone and Fenton’s reagent) [5, 14, 15], electrochemical treatment [16-22] and combination of enzyme and ultrasound treatment [23]. Treatments based on electrochemical methods have gained attention as a promising alternative to traditional chemical treatment methods for several reasons. The conditions of the electrochemical
treatment (pH, current intensity and salinity, etc.) of real textile effluent affect strongly its performance [24].

Methyl Red (MR), Methyl Orange (MO) and Methyl Yellow (MY) are acid dyes which belong to the same dye group, with difference in the functional group attached to the aromatic ring. For MR, MO and MY, we have: -COOH, -SO₄, and -H, respectively (Table 1).

In this work, the effect of different parameters: pH, current intensity, temperature, nature of the supporting electrolyte, substituent of the aromatic ring on the electro degradation rate of the three monoazo dyes were investigated to understand better the electro degradation steps of the dyes (for theoretical reasons not for direct application since they are replaced in our days by more complex ones).

**EXPERIMENTAL**

All chemicals and reagents used in this study were of analytical grade. The dyes studied (MR, MO, MY) are obtained from Merck and BDH. The stock solutions of the dyes are prepared by dissolving 25 mg of dye in 250 ml distilled water. The electro degradation of the dyes is done at room temperature (303 K), in unbuffered solution (unless indication), in presence of 0.1M KX where X is Cl, Br and I, at several current intensities, in wide range of pH with addition of H₂SO₄ (H₃PO₄) or NaOH.

Experiments were carried out in a single electrolytic cell, with working volume of 100 ml: 10 ml of dye + 10 ml of 1M KX + 10 ml acid (or base) solution of variable molarities (to have the desired pH) + 70 ml distilled water.

The electrodes and electrolysis cell characteristics are mentioned in a previous article [25]. The electrolysis is done at constant current using a Chrono-Amperostat (type CEAMD-6) from Taccusel.

The electrodegradation was followed by recording UV-VIS spectra during electrolysis of the corresponding dye, on a double beam UV-VIS Specord 200 spectrometer, Analytic Jena AG (Germany), using 1 cm quartz cells. The measurements of pH were carried out using a Toledo 220 M pH-meter. The difference in absorbance (A-A₀) at λₘₐₓ of the azo dye vs. time was used for calculation of the rate constant. All the experiments are done under stirring using magnetic stirrer.

The electro degradation was studied in function of several parameters listed above in the introduction section.

**RESULTS AND DISCUSSION**

In the conditions of this work, the order with respect to the monoazo dye via electro degradation can be considered as zero order or order one since R² values are close to each other. But order zero was selected since its R² value are nearest to 1 (Fig. 1). The plot of ln[initial rate] vs. ln[azo dye] gives a horizontal line parallel to x axis, which confirms more the selected order. The order with respect to MR via Fenton’s reagent obtained by Ashraf et al. is one [26]. The disagreement in the order may be due to the conditions of the experiment especially the method used for the degradation.

The evolution of the UV-VIS spectra during electrolysis is given in Figs. 2 and 3. The absorbance of the visible band decreases with electrolysis time. There is not any new band or any band shift in the spectra, which means probably that the degradation of the dye and its byproducts are done simultaneously.

The results obtained by other authors (from HPLC-MS analysis) showed that MO was degraded (by contact glow discharge electrolysis) into the intermediates with a small molecular mass such as phenolic compounds and carboxylic acids, so that it could be degraded more easily to CO₂ and H₂O [27].
electrolysis, 0-600 s).

Fig. 2. Variation of the UV-VIS spectra of MR during the electrodegradation. pH_2, HCl 10^{-3}M, MO 6x10^{-5}M, T 303 K, I 10 mA.

<table>
<thead>
<tr>
<th>Rate constant (M/s)</th>
<th>0.00E+00</th>
<th>5.00E-04</th>
<th>1.00E-03</th>
<th>1.50E-03</th>
<th>2.00E-03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (mA)</td>
<td>0</td>
<td>1.00E-05</td>
<td>2.00E-05</td>
<td>3.00E-05</td>
<td>4.00E-05</td>
</tr>
</tbody>
</table>

Fig. 3. Variation of the UV-VIS spectra of MY during the electrodecomposition. KCl 0.1M, MY 3x10^{-5}M, T 303 K, pH 2. (From top to down with increasing time of electrolysis, 0-600 s).

Effect of Current

The electrodegradation of the azo dyes was done in 0.1 M acetic buffer, in presence of KCl, at several currents ranging from 1 mA to 50 mA for MR and from 1 to 5 mA for MO. The results show that the decolorization rate increases linearly with current (Fig. 4). This linearity is also observed with other azo dyes [21, 25, 28]. The increase in rate degradation at higher applied current is mainly the increased production of active chlorine oxidant species at the anode. During electrolysis, the odor of hypochlorite could be noticeably smelt. The UV-VIS spectra of the electrooxidation of MR in presence of KCl are similar to that of direct oxidation with HOCl. The potential of HOCl solution decreases from 950 mV/ SCE to - 80 mV/ SCE during addition of acidic solution of MR. This result confirms clearly the indirect oxidation of dye via chlorine oxidant species.

Effect of Supporting Electrolyte (KX)

Two factors are studied in this part the nature and the concentration of salt.

KX acts in fact as strong electrolyte and as oxidant. It is interesting to study the nature of salt added on the degradation rate. The standard potential of Cl\_2/Cl\_1, Br\_2/Br\_1 and I\_2/I\_1 are 1.40, 1.10, 0.54 mV, respectively [29].

Each halide is an oxidant in the redox system X\_2/X\_- but it belongs also to a complicated system as shown below for I\_2:

\[ IO_4^- \rightarrow IO_3^- \rightarrow HOI \rightarrow I_2 \rightarrow I^- \]

+1.59(V) +1.15(V) +1.43(V) +0.63(V)

Scheme 1: Latimer diagram of iodine (in acidic medium) [29].

10 ml of 1M of the following supporting electrolytes Na\_2SO\_4, NaF, KCl, KBr and KI is added separately to the azo dye solution. The results show that the degradation rate is faster in the following order: Na\_2SO\_4 ~ NaF, KI, KCl, and KBr. In presence of Na\_2SO\_4 and NaF the electrooxidation is negligible, since H\_2O is oxidized first at Pt electrode. Therefore the direct oxidation of the azo dyes on the surface of the electrode is
ionic strength may affect the performance of the electrochemical cell. Allen et al. confirmed that the concentration of the electrolyte had a pronounced effect on cell performance resulting from the difference in ionic strengths of the electrolyte [30]. Goyal et al. have confirmed that variations in the rate constants of electrochemical oxidation of uric acid calculated for solutions containing different phosphate concentrations are due to the ionic strength of the solution [31]. On the other hand, no effect of the ionic strength was observed on the electrodegradation rate of Fluorescein [25].

The electrodegradation of MR in presence of KCl (at pH 2) with different ionic strength (addition of variable volume of 1 M Na₂SO₄ ranging from 0 to 15 ml to reactional mixture) give an increase in the rate constant by an average factor of 1.5 after each addition of 5 ml of Na₂SO₄, but unfortunately, it is not possible to apply Bronsted equation [32] to determine Z⁺ and Z⁻ (charges on A and B) since μ > 0.1 M.

**Effect of initial pH (pH₀)**

Variable pH in the wastewater helps to evaluate the effectiveness of the electrochemical cell. Szpyrkowicz

absent. On the other side I⁻, is weak oxidant with respect to Cl₂. In acidic medium, at 5 mA and at room temperature, in presence of 0.1 M KCl, 5 min is enough for total decolorization of MR, but in presence of KI - at least 3 hours.

According to the simple d rule (valid only for fast systems), the rate constant in presence of KCl must be bigger than in presence of KBr, but experimentally the degradation is faster in presence of KBr (Fig. 5), due to the presence of at least one slow system in the reactants.

The degradation of the azo dye is absent for zero concentration of KX, then it increases with the increase in KX concentration (Fig. 5). Similar results are obtained with other dyes [16, 25]. The increase in degradation rate can be explained by the increase in the amount of oxidant produced during electrolysis (Cl₂, HClO).

**Effect of ionic strength**

Wastewater from the textile industry is highly variable in ionic strength (I) and pH. A change in the

![Graph](image-url)

**Fig. 5. Effect of KX concentration on the degradation rate of MR, I 10 mA, pH 3.8, T 303 K, MR 2x10⁻⁵ M.**

![Graph](image-url)

**Fig. 6. Variation of the degradation rate of MR with pH, KCl 0.1 M, MR 2x10⁻⁵ M, T 303 K, 15 mA.**

Table 1. Structure and characteristic of azo benzene dyes: Methyl red (MR), Methyl Orange (MO) and Methyl Yellow (MY). Value in ( ) corresponds to the molar absorptivity.

<table>
<thead>
<tr>
<th>Azo dye</th>
<th>pKₐ</th>
<th>Formula</th>
<th>peak of acidic form</th>
<th>Peak of basic form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl red</td>
<td>5.1</td>
<td>C₁₅H₁₅N₇O₂</td>
<td>520 nm (61x10⁻⁵)</td>
<td>420 nm (31x10⁻⁵)</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>3.7</td>
<td>C₁₄H₁₄N₇NaO₅S</td>
<td>500 nm (24x10⁻⁵)</td>
<td>465 nm (14x10⁻⁵)</td>
</tr>
<tr>
<td>Methyl yellow</td>
<td>3.3</td>
<td>C₁₄H₁₄N₇</td>
<td>510 nm (11900)</td>
<td>440 nm (6500)</td>
</tr>
</tbody>
</table>
Table 2. Variation of the degradation rate constant with pH, KCl 0.1 M, T 303 K, I 5 mA.

<table>
<thead>
<tr>
<th>Dye</th>
<th>K at pH 1.9</th>
<th>K at pH 3</th>
<th>K at pH 6</th>
<th>K at pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>52x10^{-3}</td>
<td>3.3x10^{-3}</td>
<td>1.7x10^{-3}</td>
<td>9x10^{-4}</td>
</tr>
<tr>
<td>MR</td>
<td>8x10^{-3}</td>
<td>1.5x10^{-3}</td>
<td>0.7x10^{-3}</td>
<td>3.6x10^{-4}</td>
</tr>
<tr>
<td>MY</td>
<td>1.7x10^{-3}</td>
<td>1x10^{-3}</td>
<td>------</td>
<td>0.6x10^{-4}</td>
</tr>
</tbody>
</table>

et al. compared the treatment maintained at pH 4.5 versus treatment with no pH control (around 8.5-9.5): Electrolytic destruction of the dyes was found to be more efficient at pH 4.5 [33]. Mohan et al. compared the indirect electro-oxidation of Acid Blue 113 at pH 4, 7 and 10 [34]. They found the degradation rate to be independent of pH. However, no information about nature of buffer ions and ionic strength was provided.

The standard potentials of $X/X$ (X = Cl, Br and I) are a function of pH [35]. E° of the $X/X$ system decreases with increasing pH. The standard potential of the acid dye (MR, MO, MY) is also a function of pH, so the redox reaction between $X_2$ and the azo dyes is affected by the pH of the solution.

The experimental results show that the electro degradation of the azo dye increases with the decrease in pH° (Fig. 6).

In basic medium the degradation is slower than in acidic medium (Table 2). These results are in line with the results obtained with other textile dyes [19, 24, 25].

Faster rates in acidic medium are related to the presence of HClO and chlorine in the bulk solution. HClO has a very high oxidation potential of $E° = 1.62$ V, and it possesses higher oxidation potential than ClO . This trend may be due to unwanted side reactions with formation of ClO3 [21, 36].

Effect of Substituents

The three dyes studied have similar structure with a slight difference in the functional group attached to the aromatic ring. In the same conditions, the degradation rate increases in the following order: MY, MR and MO (Table 2). The same order is observed with MR and MO by electro Fenton process [37]. This suggests that the presence of substituent on the aromatic ring such as $SO_3^- \text{and } \text{COOH}$ favors the degradation.

Effect of Temperature

The degradation rate at different temperatures shows that the rate constant at high temperature (309 K and 313 K) is lower than that at 293 K (Fig. 7). This is due to the liberation of $Cl_2$ from aqueous solutions at higher temperature. Similar result is also obtained with the degradation of the azo dye Orange II using Fenton’s reagent [15] and with Fluorescein [25].

CONCLUSIONS

Indirect electrochemical oxidation of monoazo benzene dye in the presence of several supporting electrolyte was investigated. The direct electro decomposition of the azo dye at the surface of the Pt. electrode is negligible. Low pH, low temperature, high current and high concentration of the supporting electrolyte increases individually the degradation rate. The electrochemical degradation fits better with zero order. The degradation rate increases with respect to the azo dye in the following order: MY, MR, MO. Also the rate increases with respect to the supporting electrolyte in the following order: $Na_2SO_4 \sim NaF, KI, KCl, \text{and } KBr$.

Acknowledgements

Thanks to Prof. Dr. H.H. Hammud for his help and to Miss M. Serhal for the preparation of the chemicals solutions.

REFERENCES