Degradation mechanism of Methyl Orange by electrochemical process on RuO\textsubscript{x}–PdO/Ti electrode
Lin Du, Jin Wu, Song Qin and Changwei Hu

ABSTRACT
The electrochemical degradation of Methyl Orange in 0.1 M NaCl solution over RuO\textsubscript{x}–PdO/Ti anode was investigated. Chemical oxygen demand (COD), ion chromatography (IC), Fourier Transform Infrared Spectroscopy (FTIR) and Gas chromatography-mass spectrometry (GC-MS) were employed to detect the intermediates formed during the electrochemical degradation. In the present reaction system, Methyl Orange could be effectively degraded. After 1 h treatment, the discoloration could reach 97.9% with COD removal of 57.6%. The results indicated that in the presence of chloride, the electrolysis was able to oxidise the dye with partial mineralisation of carbon, nitrogen and sulfur into CO\textsubscript{2}, NO\textsubscript{3}/CO\textsubscript{3} and SO\textsubscript{4}/CO\textsubscript{4}, respectively. After 8 h electrolysis, 62% of sulfur contained in Methyl Orange was transformed to SO\textsubscript{4}, and 17.6% of nitrogen changed to NO\textsubscript{3}. The intermediates during electroprocess were detected to be low molecular weight compounds, chlorinated compounds, derivatives of benzene and long chain alkanes. Based on these data, a possible degradation mechanism of Methyl Orange was proposed.

Key words | dye wastewater, electrochemical degradation, intermediates

INTRODUCTION
Industrial dye wastewater from textile and photographic industry is a principal source of environmental contamination. Large amounts of dye were released into the environment accompanied by dissolved inorganic salts, surfactants, dispersing agents, and other organics. Due to the increasing environmental pollution and the establishment of stringent standards for rejecting wastewaters, developed techniques are urgently needed to purify the industrial wastewater.

Many methods have been applied to dye wastewater treatments, such as physical methods (Gupt & Suhas 2009), biological treatment (Baban et al. 2010; González-Martínez et al. 2010), chemical degradation including ozonation (Constantel et al. 2009), Fenton reaction (Rodrigues et al. 2009; Arslan-Alaton et al. 2010), electrochemical treatment (Raghu et al. 2009), photochemical treatment (Chakrabarti et al. 2008; Lv et al. 2009) and so on.

Among these technologies, electrochemical methods have been studied extensively in the past few years. Vaghela et al. (Vaghela et al. 2005) investigated the use of dimensional stable anode in the treatment of industrial azo dye effluent containing chiefly reactive dyes and proved that electrochemical method was very effective. Faouzi et al. (2007) found that Alizarin Red S was not only successfully decolourised but also totally degraded and mineralised by anodic oxidation at boron-doped diamond electrode in sulfuric medium.

Most investigations about dye degradation, however, focused on the information on discoloration, COD or TOC removal, including our previous work about water treatment using RuO\textsubscript{x}–PdO/Ti anode (Wu et al. 2007; Dai et al. 2008). In contrast, the mechanistic details of dye degradation and the intermediates in the electrochemical process were scarcely investigated. Therefore, in the present study, an attempt was made to study the mechanism of electrochemical degradation. Since a large amount of dissolved sodium chloride was usually contained in the real dyeing contaminants, the...
present electrolysis experiments were carried out using RuO$_x$–PdO/Ti anode in a chloride medium for discussing the mechanism of degradation. In this study the electrochemical oxidation was anodic oxidation (Brillas et al. 2009) in which the dye might be destroyed by the direct oxidation of the pollutant at the anode and chlorine-based oxidants generated in NaCl solution (Wang et al. 2009).

**METHODS**

**Instruments and reagents**

The experimental instruments and reagents used are listed in Table 1.

**Preparation of RuO$_x$–PdO/Ti electrode**

The RuO$_x$–PdO/Ti electrode was prepared by coating and thermal decomposition, according to the report of Dai et al. (2008).

**Electrochemical system**

Electrochemical degradation was carried out in an undivided electrolytic cell at RuO$_x$–PdO/Ti anode against Ti mesh cathode, both with the area of 56 cm$^2$ (40 mm × 70 mm × 0.5 mm), under galvanostatic condition with the current of 0.05 A. The anode positioned vertically with an interelectrode gap of 1 cm to the cathode. MO solution (0.5 L) with an initial concentration of 100 mg/L and 0.1 M NaCl as electrolyte was sampled during the reaction. The pH of the solution was 6.4 without any adjustment. The dye solution was stirred by a magnetic stirrer at the same time.

**Analytical methods**

The concentration of the Methyl Orange in the solution was monitored using a UV-VIS spectrophotometer at 465 nm, corresponding to the maximum absorption wavelength of MO in visible region. The chemical oxygen demand (COD) during degradation was determined by microwave digestion method as described in Standard Method.

Samples after a certain period of reaction time were prepared by two methods before being injected into the GC-MS. In the first method, ethyl ether was used to extract organic compounds and the layer of ethyl ether was collected. Then it was condensed to about 1 mL. In the second method, the sample was concentrated under reduced pressure at a temperature below 323 K. The residue was finally dissolved in 0.5 ml of methanol for GC-MS analysis. The GC-MS data included the information got from both methods.

For the FTIR spectra detection, the dry residue was obtained by the second method, and supported on a KBr pellet before FTIR measurement.

The quantity of the SO$_4^{2−}$ and NO$_3^{−}$ formed in the electrocatalytic degradation process were assayed by ion chromatography.

**RESULTS AND DISCUSSION**

**Electrodegradation of MO**

The concentration changes and COD removal of MO during the electrochemical degradation process were displayed in Figure 1. The discoloration reached 97.9% after 1 h treatment, suggesting that the electrochemical process could break most of the MO molecules and make them decompose.

<table>
<thead>
<tr>
<th>Name</th>
<th>Purity grade/Type</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium plate</td>
<td>TA1</td>
<td>Chengdu Guangxu Titanium Co., Ltd. (China)</td>
</tr>
<tr>
<td>Methyl Orange</td>
<td>AR</td>
<td>Chengdu Kelong Chemical Reagent Factory (China)</td>
</tr>
<tr>
<td>RuCl$_3$, nH$_2$O, PdCl$_2$</td>
<td>AR</td>
<td>Kunming Institute of Precious Metals (China)</td>
</tr>
<tr>
<td>UV-VIS spectrophotometer</td>
<td>U-722</td>
<td>Cny Pricision Instruments Co., Ltd. (China)</td>
</tr>
<tr>
<td>Gas chromatography-mass spectrometry</td>
<td>Agilent 6890</td>
<td>Agilent Technologies Co., Ltd. (U.S.A.)</td>
</tr>
<tr>
<td>Fourier Transform Infrared Spectroscopy</td>
<td>NEXUS 670</td>
<td>Thermo Nicolet Corporation (U.S.A.)</td>
</tr>
<tr>
<td>Ion Chromatography</td>
<td>ICS-90</td>
<td>Dionex Corporation (U.S.A.)</td>
</tr>
</tbody>
</table>
effectively. At the same time, 55.2% COD was removed, and COD removal increased slowly to 77.7% after 8 h treatment. However, there was no obvious change of the COD removal in the successive 4 h. It was assumed that the possible intermediates might be resistant to the electrodegradation and therefore still existed even with prolonged time of reaction. As a result, MO could be partially mineralised. In the later section, this was further confirmed by the FTIR and GC-MS analyses.

The electricity consumption was 3.2 wh/g (MO) for 90% dye removal and the cost of treating 1 g dye was $0.0147 (electricity: 0.0004; chemical: 0.0143). The electricity consumption was a little higher compared with other reports (Sanromán et al. 2004: 3 wh/g MO; Sirés et al. 2010: 1.66 wh/g MO), but the cost was much lower since high concentration of NaCl and pure O₂ was used in their work respectively (Sanromán et al. 2004: $0.143/ g MO; Sirés et al. 2010: $ 0.0442/ g MO).

**Formation of inorganic ions**

In order to investigate the degradation of MO, some inorganic ions generated from the degradation were measured. Only SO₄²⁻ and NO₃⁻ were detected in the sample solution by IC analysis. The possibly formed NH₄⁺ ion could not be found, because of the oxidation in the electrochemical process in NaCl solution according to the “fold-point chloridise” (Song et al. 2006).

SO₄²⁻ ion was the product which might result from the attack on the sulfonyl group of MO, while NO₃⁻ was formed from the nitrogen element of MO molecule. The formation of these two inorganic ions with exposure time was presented in Figure 2. The increasing amount of these ions showed that more bonds connected to sulfur and nitrogen were cleaved as the experiment time prolonged. 12 h later, the amounts of SO₄²⁻ and NO₃⁻ were 0.199 mmol/L and 0.137 mmol/L, respectively, showing that 62% of the total sulfur was transformed to SO₄²⁻, while 14.9% of total nitrogen element was present in the form of NO₃⁻. FTIR analysis also confirmed that most of the sulfonyl group disappeared after degradation, whereas 38% of sulfur might still exist in the intermediates containing S elements. Compared with the evolution of sulfur element, less percentage of nitrogen element was converted to NO₃⁻, which might be caused by the formation of N₂. The amount of NO₃⁻ reached its maximum value at 6 h, which was 2 h earlier than that of SO₄²⁻, showing that the mineralisation of sulfur compounds could not be achieved as easily as nitrogen compounds.

As shown in Figure 2 and Figure 1, COD removal reached the maximum value at 8 h while the amount of SO₄²⁻ ion formed also increased to the highest amount after 8 h treatment, showing that COD removal likely depended on the disulfuration process to some extent.

This might be due to the fact that the C–S bond was advantageously attacked by oxidants over other bonds in the degradation. The work of Li et al. (2004) showed that the C–S bond was firstly attacked and then followed the cleavage of other bonds, such as N¼N, C–C, C–N etc. in photocatalytic degradation. So the attacking sequence might be the same in the present system, and after
disulfuration attack of groups without S atom occurred, causing continuous COD removal. However, this C–S bond breakage might be slow.

Formation of Intermediates

FTIR data

The MO solutions before and after electrodegradation were monitored by FTIR spectroscopic method to investigate the intermediate formation. Figure 3 showed the FTIR spectra for samples before degradation and after 48 h treatment.

After degradation, the characteristic absorption peaks of phenyl at 1,606, 1,520, 1,446 cm\(^{-1}\) and the band at 1,367 cm\(^{-1}\) linked to the C–N bond of aromatic tertiary (Ar–NMe\(_2\)) disappeared (Sun et al. 2006). This suggested that the phenyl ring and C-N bond were attacked and cleaved during the electrodegradation. The peaks at 1,421 cm\(^{-1}\) attributed to azo bond adsorption vanished after degradation. This demonstrated that the rupture of azo bond occurred in the process, which resulted in the colour removal of MO. The peak at 1,039 cm\(^{-1}\) attributed to the sulfonyl group (Sun et al. 2006) was also absent after degradation, indicating that sulfonyl group disappeared after treatment. This the sulfonyl group disappearance was also confirmed by the generation of SO\(_4^{2-}\) ion obtained from IC as mentioned above.

The absorption peaks of C–H bonds of di-substituted benzene at 818 and 845 cm\(^{-1}\) shifted to 835 cm\(^{-1}\) and 876 cm\(^{-1}\). The peaks at 697 and 623 cm\(^{-1}\) changed to 680 and 621 cm\(^{-1}\). This shift of absorption might have resulted from the structural changes to which the corresponding functional group formerly connected.

The newly formed band at 1,643 cm\(^{-1}\) after degradation was due to the absorption of the carbonyl group (Li et al. 2006). The wave number is lower than that of normal C=O compound, because of the conjugate effect of C=O and C=C of the phenyl, indicating that intermediates with conjugate structure and carbonyl group might be generated after treatment. Low intensity absorption at 799 cm\(^{-1}\) was a newly formed peak which could be attributed to the [CH\(_2\)]\(_n\) wagging vibration (Qin et al. 1991). Besides, the additional peaks at 1,383 cm\(^{-1}\) along with the shoulder at 1,450 cm\(^{-1}\) were attributed to C–H bending stretching of alkanes.

The data from FTIR spectra provided the evidence to support that MO was attacked at several sites, including the sulfonyl group, C-N bond, and phenyl group, and other compounds like long-chain alkanes and compounds with carbonyl group were formed.

GC-MS data

The formation of the above mentioned intermediates in the degradation process was further confirmed by GC-MS technique. The detected intermediates formed at different degradation time were listed in Table 2, including low molecular weight compounds (A, B, C, D), chlorinated compound (H), benzene derivatives (E, F, G, I, J) and long chain alkane compounds (K).

The species containing C=O group with adsorption peak around 1,650 cm\(^{-1}\) and long chain alkanes with the absorption at 799 and 1,380 cm\(^{-1}\) were confirmed by GC-MS. Compounds containing S element were not detected, though they still existed in the solution. This might be caused by their instability.

<table>
<thead>
<tr>
<th>Degradation time</th>
<th>Intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>30 min</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>1 h</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>2 h</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>4 h</td>
<td><img src="image5.png" alt="Structure" /></td>
</tr>
<tr>
<td>12 h, 24 h</td>
<td><img src="image6.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
The formation of chlorinated compound \( H \) provided strong evidence that, during electrochemical process with NaCl as electrolyte, chlorine was involved in the degradation reaction to form chlorine-substituted byproduct which may lead to secondary pollution. This was different from the report of Rajknmr et al. (Rajknmr et al. 2007) in which no chlorinated compounds were found in the electrodegradation of dye wastewater. This discrepancy might be caused by the difference of selected dye and electrode materials, which might result in the variation of electrolytic mechanism. It could be easily identified that the appearance of compound \( H \) was directly formed from the break of N–C bond of (N–ArNC\(_2\)H\(_6\)) during the attack of active chlorine, a very strong oxidant formed in the electrochemical degradation. This showed that active chlorine was involved in the degradation reaction in the way of attacking substrate, breaking the molecule structure.

Also uniquely found in the experiment was the formation of long-chain alkanes. In order to eliminate the influence of the impurity from the MO, sample before treatment was analysed by GC-MS and no alkanes were detected. Since the alkane chain was very long and had high saturation, this species should not have arisen from the cleavage of phenyl group of the Methyl Orange in the process. Therefore, it is suspected that alkane species might be generated from the methyl radicals during the electrolysis.

As hydroxyl radicals produced by the electro degradation were electrophilic oxidants, the amino group, an electrophile site, could be attacked by OH• resulting in the formation of methyl radicals. The reaction could be achieved by the loss of CH\(_3\)• from an unstable nitrogen radical which was formed by the attack of OH• on the electrophile nitrogen atom. The possible mechanism was depicted in scheme 1.

The methyl radicals formed in our experiment underwent collision reaction to produce the long-chain alkanes.

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\text{Compound J containing two phenyl groups without nitrogen element was probably generated by the polymerisation of some intermediates. This made it clear that compounds formed in the degradation could polymerise to generate other complex compounds.}
\]

**Electrochemical degradation pathway of MO**

Based on the above results, the degradation pathway of Methyl Orange was proposed as shown in Figure 4.

Three steps were involved in the mechanism:

1. MO molecule was attacked at the site of sulfonyl group, azo bond, and phenyl group by active chlorine and hydroxyl radical, consequently forming methyl radicals CH\(_3\)•, chlorinated compounds, and other intermediates with S or N, some of which were not detected by GC-MS. SO\(_4^{2-}\) and N\(_2\) could be formed from part of S and N elements contained in MO.

2. The intermediates formed in the first step could polymerise or further degrade. The methyl radicals collided and generated long-chain alkanes, or may also form other low molecular weight compounds. The chlorinated compounds and other intermediates formed may either be attacked to further degrade or react with active radicals (CH\(_3\)•, Cl•OH•) to form benzene derives which could polymerise to form more complex compounds, such as J.

3. The third step involved the further oxidation of the intermediates formed from the above to produce CO\(_2\), H\(_2\)O and inorganic ions until total mineralisation.

**CONCLUSIONS**

Effective destruction of Methyl Orange was achieved by electrochemical degradation using RuO\(_x\)–PdO/Ti electrode in the presence of chloride. The COD removal and the change of dye concentration were investigated. The mineralization of Methyl Orange showed that some organic compounds resistant to the electrodegradation were formed after the chromospheres group of MO cleavage and still existed even with prolonged reaction time. SO\(_4^{2-}\) and NO\(_3^-\) were detected during the degradation process. The intermediates during the degradation were composed of low molecular weight compounds, chlorinated organic compounds, aromatic compounds, and long-chain alkanes, which could be further oxidized slowly to CO\(_2\). Details obtained from the FTIR, GC-MS, and Ion spectroscope showed that three degradation steps involved in the Methyl Orange electrooxidation. Firstly, MO molecule was attacked at the site of sulfonyl group, azo bond, and phenyl group by active chlorine and hydroxyl radical to form chlorinated compounds and other organics. Secondly, the intermediates formed in the first step could polymerize to form complex compounds such as benzene derives or long-chain alkanes or they may further degrade. Finally, all those organics could be mineralized to generate CO\(_2\), H\(_2\)O and inorganic ions.
ACKNOWLEDGEMENTS

The project is financially supported by the Teaching and Research Award Program for outstanding Young Teachers in Higher Education Institution of MOE, P.R.C. The characterisation of the anodes from Analytical and Testing Center of Sichuan University is greatly appreciated.

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