Heterogeneous electro-Fenton oxidation of azo dye methyl orange catalyzed by magnetic Fe₃O₄ nanoparticles
Hao Jiang, Yabing Sun, Jingwei Feng and Jian Wang

ABSTRACT

Azo dye methyl orange (MO) degradation by heterogeneous electro-Fenton (EF) with a magnetic nano-Fe₃O₄ catalyst was investigated. In this study, Fe₃O₄ was synthesized by a coprecipitation method and characterized by X-ray diffraction and scanning electron microscopy. The influences of the main operating parameters such as current density, pH, catalyst dosage and aeration rate were studied. The results revealed that higher current density, catalyst dosage and aeration rate facilitated the degradation of MO, whereas the degradation efficiency of MO was decreased with an increase in the initial pH. After 90 min EF process, the volume of 500 mL, the initial concentration of 50 mg L⁻¹ MO solution could be degraded by 86.6% with the addition of 1 g L⁻¹ Fe₃O₄ under the current density of 10 mA cm⁻² and pH 3, compared with 69.5% for the electrolytic process alone. Meanwhile, a total organic carbon removal of 32% was obtained, up to 35.5 mg L⁻¹ accumulated H₂O₂ and less than 3.5 mg L⁻¹ Fe leaching were detected. Moreover, based on the results of natural bond orbital (at B3LYP/6-311G (d, p)) and liquid chromatograph-triple quadrupole mass spectrometer analysis, nine intermediates were identified and the proposed degradation pathways were investigated.

Key words | electro-Fenton process, H₂O₂, iron leaching, magnetic Fe₃O₄ nanoparticles, methyl orange

INTRODUCTION

Azo dyes, a class of organic compounds with aryl connected to both ends of an azo group (–N–N–), are a kind of synthetic dyes which are not only widely utilized in the printing and dyeing process of textile for a variety of natural and synthetic fibers dyeing and printing, but also used as colorant in plastics, rubber and paint, etc. (Kariminiaae-Hamedaani et al. 2007; Pandey et al. 2007). Due to it being a highly structured polymer with low reactivity and biodegradation of azo dyes, this type of compound is resistant to degradation in wastewater treatment (Konstantinou & Albanis 2004; Zhang et al. 2012). Under certain special conditions, azo dyes are able of decomposing to produce more than 20 kinds of carcinogenic aromatic amines, which will change the DNA structures of the human body through the activation inducing lesions and cancer (Song et al. 2007; Carneiro et al. 2010). Methyl orange (MO), a typical azo dye with single azo groups, has often been selected as a model contaminant in numerous investigations (Huang et al. 2012; Ramírez et al. 2013; Gupta & Pal 2014) and is extensively utilized in chemical, paper and textile industries.

Nowadays, advanced oxidation processes (AOPs) have been considered as a powerful oxidative technique for treating organic and inorganic pollutants in aqueous phases, especially for recalcitrant and biorefractory organic contaminants (Matilainen & Sillanpaa 2010; Xin et al. 2015). AOPs are based on the in situ generation of hydroxyl radicals (•OH), a highly reactive (oxidation potential: 2.8 V) and non-selective chemical oxidant. Among the AOPs, Fenton and electro-Fenton (EF) techniques have become the favored process because of their high performance (Iglesias et al. 2014; Xu & Wang 2015), adopting ferrous iron (Fe²⁺) as a homogeneous catalyst to activate hydrogen peroxide for •OH generation through a Haber-Weiss mechanism (Equation (1)).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}
\]
However, there exist several drawbacks limiting application in the current traditional homogeneous Fenton process, as follows. (i) A strict pH range (pH 3-4) is required in order to prevent Fe$^{2+}$ precipitation and ensure reaction Equation (1) proceeding efficiently. (ii) It is rather difficult to separate and dispose of high quantities of iron sludge produced after treatment. (iii) The low regeneration rate of Fe$^{2+}$ and large amount of H$_2$O$_2$ reagent consumed.

Based on the above mentioned problems of the traditional homogeneous Fenton process, more and more attention is gradually being paid to the heterogeneous EF because of its own unique advantages as a promissory alternative technology. H$_2$O$_2$ can be continuously produced in situ from the two-electron reduction of O$_2$ (Equation (2)) and Fe$^{2+}$ that can be quickly regenerated (Equation (3)) via the reduction of Fe$^{3+}$ on the cathode under acidic conditions.

$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$$  (2)

$$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$$  (3)

The heterogeneous EF system, catalyzed by heterogeneous Fenton-like catalysts such as magnetic Fe$_3$O$_4$ nanoparticles, can degrade pollutants efficiently in a wider pH range with less iron sludge formation. Among the various heterogeneous catalysts applied in Fenton reactions, magnetic Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$ MNPs) have shown high catalytic activity for the oxidation of contaminants with minimal soluble Fe$^{2+}$ leaching. The octahedral site in the magnetite structure can easily accommodate both Fe$^{2+}$ and Fe$^{3+}$, which means that Fe$^{3+}$ can be reversibly oxidized and reduced back through electron transfer between Fe$^{2+}$ and Fe$^{3+}$ in the same structure. In addition, the catalyst can be easily separated from the reaction medium by external magnetic field.

In the current study, Fe$_3$O$_4$ MNPs were synthesized and characterized. Applicability of Fe$_3$O$_4$ MNPs as a heterogeneous EF catalyst in the degradation of MO was investigated. The influences of the main operating parameters such as current density, pH, catalyst dosage and aeration rate were studied. The changes in total organic carbon (TOC) and UV–Vis absorption spectra were examined. Furthermore, this paper discusses the possible degradation mechanism and identifies the degradation intermediates of MO using a liquid chromatograph-triple quadrupole mass spectrometer (LC-QqQ-MS) combined with theoretical calculation of Gaussian 09 program.

### EXPERIMENTAL

#### Materials

MO (analytical standard, purity grade 99%) was purchased from Aladdin Inc. Methanol used in the analysis was high-performance liquid chromatography grade. Other chemicals were all analytical reagent grade. FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O were supplied by Sinopharm Chemical Reagent Co., Ltd. Ammonia solution (25%) and Na$_2$SO$_4$ was purchased from Nanjing Chemical Reagent Co., Ltd. All solutions were prepared with ultrapure water obtained from using an ultrapure water system (Milli-Q Gradient, USA).

#### Experimental process

The schematic diagram of the EF reactor is shown in Figure 1. The EF degradation of MO was carried out in an undivided electrolytic cell. RuO$_2$/Ti flake (5 cm × 9 cm × 0.1 cm) was used as the anode and C-PTFE flake, the mass ratio of the carbon black and PTFE was 3:1 in the mixture and calcination 1 h at 350 °C, was used as the cathode with the same dimension. The distance between the anode and cathode was 5 cm, direct current was provided by DC regulated power supply (TPR, Hong Kong LongWei Instrument Co., Ltd, China) and the voltage and current could be accurately regulated and measured. Air was dispersed at the bottom of the cathode through an electromagnetic air pump (ACO-002, Zhejiang Dense Industrial Co., Ltd, China), and aeration rate was controlled by a rotameter (LZB-4, Shanghai Splendor Instrument and Meter Plant, China).

Fifty milligrams per litre of MO solution was prepared for the degradation experiment, in which the conductivity was only 10.38 μS cm$^{-1}$. To improve the conductivity of MO solutions and the reaction system atmosphere of EF, 500 mL of MO solution containing 50 mmol L$^{-1}$ Na$_2$SO$_4$ was added into the reactor and stirred for all the experiments except...
determination of H$_2$O$_2$ concentration; the increase of conductivity was beneficial to reduce the extra power loss. A series of Fenton experiments were performed on different operating parameters, including current density (5, 10, 20, 40 mA cm$^{-2}$), pH (2, 3, 5, 7, 9.5), catalyst dosage (0, 0.4, 1, 2 g L$^{-1}$) and aeration rate (0, 0.75, 1.5, 3.5, 5 L min$^{-1}$). Samples of MO solution taken out of about 3 mL every 10 min were measured for absorbance at $\lambda = 505$ nm on a spectrophotometer. The pH value of solutions was adjusted using diluted solutions of H$_2$SO$_4$ or NaOH. For determination of dissolved Fe concentration and TOC, samples of MO solution were taken out every 15 min for the two sets of experiments under the same conditions. As for determination of H$_2$O$_2$ accumulated concentration, taking into account that the color of dye MO solution would interfere with the quantification of H$_2$O$_2$, MO solution was substituted for the solution at 400 nm was measured. A blank, consisting of 2 mL of ultrapure water, 4 mL of the H$_2$SO$_4$ solution and 2 mL of the aqueous sample and 4 mL (5 mol L$^{-1}$) of H$_2$SO$_4$ solution were pipetted into 25 mL color comparison tubes, after fully shaking, the other 4 mL (3 mol L$^{-1}$) of the titanium reagent were pipetted into the mixture and shake. After standing for 10 min, the absorbance of the solution at 400 nm was measured. A blank, consisting of 2 mL of ultrapure water, 4 mL of the H$_2$SO$_4$ solution and the titanium reagent and 4 mL of the titanium reagent, was also measured. Then the H$_2$O$_2$ concentration was calibrated with known standard stock H$_2$O$_2$.

The Fe leaching concentration of catalyst was detected using an atomic absorption spectrophotometer (Thermo Solar M6, USA) with a hollow cathode lamp (Thermo Fe, USA). TOC was determined on a TOC analyzer (OI Aurora 1030D, USA). The UV–Vis absorption spectra changes of MO solution during the reaction were measured by UV–Vis spectrophotometer (Shimadzu UV-2450, Japan) at a wavelength ranging from 200 to 700 nm. The pH value of the solution was measured by a pH meter (PHS-3B, Shanghai Kangyi Instrument Co., Ltd, China).

Under acidic conditions, both the geometric optimization of the spatial structure and space charge distribution of MO were analyzed and calculated by Gaussian 09 software at B3LYP/6-311G (d, p) level. The identification of MO and its degradation intermediates were performed by a LC-QqQ-MS (Agilent 1290 Infinity LC/ Agilent 6460 QqQ MS, USA) equipped with Synchros C18 column (250 mm × 4.6 mm i.d. 5 μm, Thermo, USA) at 30 °C and the mobile phase was composed of 20% methanol and 80% ultrapure water, at a flow rate of 0.2 mL min$^{-1}$. The samples were filtered through 0.45 μm filter membrane and the volume injected was 10 μL. The MS was operated in the positive mode with electrospray source ionization by applying an interface voltage of 4.5 kV, and the full scan acquisition of $m/z$ ranged from 50 to 600.

### Synthesis of nanosize Fe$_3$O$_4$

Magnetite nanoparticles Fe$_3$O$_4$ (Fe$_3$O$_4$ MNPs) were synthesized with the method of chemical coprecipitation (Niu et al. 2012). FeCl$_3$·6H$_2$O (5.2 g) and FeCl$_2$·4H$_2$O (2 g) were dissolved in 100 mL of deionized water at 80 °C by the usage of a constant temperature magnetic agitator. Subsequently, the cooled mixture was stirred by an electric mixer and 10 mL ammonia solution (25%) was added rapidly into the reaction solution. Continuous stirring was needed for 30 min until the reaction was completed. The precipitates were separated from the solution by a powerful magnet and washed with deionized water several times until the supernatant was neutral. To prevent the oxidation of Fe$_3$O$_4$ and avoid the formation of Fe$_2$O$_3$ impurity in the product, the obtained Fe$_3$O$_4$ MNPs were dried under nitrogen protection at 40 °C overnight.

### Characterization

The crystal phase of Fe$_3$O$_4$ was investigated by X-ray diffraction (XRD) (ARL X'TRA, Switzerland) equipped with monochromatic light-intensity Cu Kα radiation ($\lambda = 1.540562$ Å, 40 kV, 40 mA), in the range from 10° to 80° at a scanning rate of 8° min$^{-1}$. The surface morphologies and microstructures were characterized using a scanning electron microscopy (SEM) (Hitachi, S-3400N II) working at 150 kV accelerating voltage.

### Analysis methods

The degradation efficiency of MO was measured using a UV–Vis spectrophotometer (UV-5100, Shanghai Metash Instruments Co., Ltd, China). The absorbance of MO solution was monitored at a wavelength of 505 nm. The degradation efficiency of MO was evaluated as in Equation (4):

$$\text{Degradation(%) = } \frac{A_0 - A_t}{A_0} \times 100\% \quad (4)$$

where $A_0$ and $A_t$ are the initial absorbance of MO and the absorbance at a certain oxidation time respectively.

The concentration of H$_2$O$_2$ was measured by titanium potassium oxalate (IV) spectrophotometric method (Sellers 1980; Kormann et al. 1988). Briefly, 2 mL of the aqueous sample and 4 mL (5 mol L$^{-1}$) of H$_2$SO$_4$ solution were pipetted into 25 mL color comparison tubes, after fully shaking, the other 4 mL (3 mol L$^{-1}$) of the titanium reagent were pipetted into the mixture and shake. After standing for 10 min, the absorbance of the solution at 400 nm was measured. A blank, consisting of 2 mL of ultrapure water, 4 mL of the H$_2$SO$_4$ solution and the titanium reagent and 4 mL of the titanium reagent, was also measured. Then the H$_2$O$_2$ concentration was calibrated with known standard stock H$_2$O$_2$. 

The Fe leaching concentration of catalyst was detected using an atomic absorption spectrophotometer (Thermo Solar M6, USA) with a hollow cathode lamp (Thermo Fe, USA). TOC was determined on a TOC analyzer (OI Aurora 1030D, USA). The UV–Vis absorption spectra changes of MO solution during the reaction were measured by UV–Vis spectrophotometer (Shimadzu UV-2450, Japan) at a wavelength ranging from 200 to 700 nm. The pH value of the solution was measured by a pH meter (PHS-3B, Shanghai Kangyi Instrument Co., Ltd, China).
RESULTS AND DISCUSSION

Characterization of the catalysts

The XRD patterns of the synthesized catalysts are shown in Figure 2. It is noteworthy that the major diffraction peaks at 2θ values 30.06°, 35.42°, 43.03°, 53.54°, 56.88° and 62.52° could be indexed to the (220), (311), (400), (422), (511) and (440) cubic spinel planes of Fe3O4 (JCPDS No. 19-0629). No other miscellaneous diffraction peaks were detected in the XRD patterns, indicating that the Fe3O4 nanoparticles synthesized were pure with a highly crystalline nature. The SEM images (Figure 3) of morphology and microstructure about Fe3O4 certified that the Fe3O4 MNPs were quasi-spherical with diameters ranging from 200 to 300 nm.

Degradation properties

Effect of current density on MO degradation

In the EF process, the current intensity is a key parameter to the generation of H2O2 at the cathode (Ozcan et al. 2009). The effect of current density on the MO degradation is demonstrated in Figure 4(a). The degradation efficiency increased dramatically from 67.3% to 83.4% within 60 min when the current density rose from 5 to 20 mA cm⁻². As shown in Figure 4(b), higher current intensity increased the accumulated concentration of H2O2 (Equation (2)), thus increasing the number of •OH in the electrolyte (Labiad et al. 2013), which was conducive to the degradation of MO. Furthermore, with current intensity increased, higher regeneration rate of Fe²⁺ from Fe³⁺ (Equation (3)) could be obtained at the cathode (Ozcan et al. 2009). However, there was no significant improvement in degradation efficiency of MO and accumulated concentration of H2O2 with further increase in current density from 20 to 40 mA cm⁻², which could be ascribed to some side reactions such as four-electron reduction of O₂ (Equation (5)) and further reduction of H₂O₂ at the cathode (Equation (6)) or H₂O₂ decomposition at the anode (Equations (7) and (8)) (Xia et al. 2015). In addition, the decrease of H₂O₂ concentration at contact times higher than 60 min slowed down the removal rate of MO.

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  

(5)
\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \]  
\[ \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ + e^- \]  
\[ \text{HO}_2^- \rightarrow \text{O}_2 + \text{H}^+ + e^- \]  

**Effect of pH on MO degradation**

Using low current density was beneficial to prolong the service life of the electrodes. Therefore, the current density was set to 10 mA cm\(^{-2}\) in the following experiments. Figure 5(a) shows the effect of different pH values on MO degradation. As seen in Figure 5(a), the degradation efficiency of MO decreased significantly with the increase of pH of solution, higher degradation rate occurred in acidic circumstances than in alkaline. At pH 2 and 3, 94.7% and 86% MO degradation was obtained after 90 min, but only 67.5% and 68.6% MO degradation for pH 7 and 9.5, respectively. Furthermore, the accumulated concentration of H\(_2\)O\(_2\) and the concentration of iron leaching were determined at pH varying from 3 to 9.5 (Figure 5(b)). There are conducive to the production of H\(_2\)O\(_2\) and dissolution of iron from catalyst in acidic circumstances. The decrease of MO degradation efficiency with the pH increased can be attributed to the inhibition of the homogeneous Fenton process because of the reduction of H\(_2\)O\(_2\) concentration and dissolved concentration of iron in the solution (He et al. 2014; Hammouda et al. 2015; Seyed Dorraji et al. 2015). Moreover, reducing the amount of -OH catalyzed by Fe\(_3\)O\(_4\) MNPs on the catalyst surface (Hu et al. 2011) and self-decomposition of H\(_2\)O\(_2\) also...
have an effect on the degradation of MO at high pH (Seyed Dorraji et al. 2015).

**Effect of catalyst dosage on MO degradation**

The influence of Fe$_3$O$_4$ MNP loading on the heterogeneous Fenton degradation of MO was investigated; the result is shown in Figure 6(a). The degradation efficiency of MO improved with catalyst dosage increasing. Compared with 69.5% MO being removed by the electrolytic reaction at current density 10 mA cm$^{-2}$, 78.9% and 90.6% MO was degraded respectively with Fe$_3$O$_4$ MNPs loading increasing from 0.4 to 2.0 g L$^{-1}$ within 90 min. The increased Fe$_3$O$_4$ MNP content did provide positive effects, which is due to the increasing

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**Figure 6** | Effect of catalyst dosage on (a) degradation efficiency of MO; (b) concentration of iron leaching (500 mL, initial MO concentration = 50 mg L$^{-1}$, current density = 10 mA cm$^{-2}$, pH = 3, aeration rate = 1.5 L min$^{-1}$).

**Figure 7** | Effect of aeration rate on (a) degradation efficiency of MO; (b) accumulated concentration of H$_2$O$_2$ (500 mL, initial MO concentration = 50 mg L$^{-1}$, current density = 10 mA cm$^{-2}$, initial pH = 3, Fe$_3$O$_4$ MNPs dosage = 1 g L$^{-1}$).

**Figure 8** | UV-Vis absorption spectra changes of MO in the EF system (500 mL, initial MO concentration = 50 mg L$^{-1}$, current density = 10 mA cm$^{-2}$, initial pH = 3, Fe$_3$O$_4$ MNPs dosage = 1 g L$^{-1}$, aeration rate = 1.5 L min$^{-1}$).
amount of active sites on the catalyst surface accelerating decomposition of H₂O₂ to form \( \cdot \)OH and enhanced leaching of iron from the catalyst surface (Figure 6(b)) (Kim et al. 2016). However, only slightly improvement could be observed for the presence of 4 g L⁻¹ Fe₃O₄ MNPs in the medium, which was ascribed to the incidental agglomeration of excessive Fe₃O₄ MNPs with large specific surface area decreasing the accessible surface active sites (Xu & Wang 2012).

Effect of aeration rate on MO degradation

The effects of aeration rate on the degradation of MO in the EF system are presented in Figure 7(a). The degradation efficiency of MO attained 81.1%, 86.6% and 92.6% at aeration rate 0.75, 1.5 and 3.5 L min⁻¹ in 90 min, respectively; far above the case without aeration. This result indicated that not only could increasing aeration rate enhance the mass transfer rate of the pumped air, but also improve dissolved oxygen (DO) in solution. It is common sense that H₂O₂ is generated by the reduction of DO on the cathode surface as for the cathodic EF reaction adequate DO was conducive to H₂O₂ electro-generation (Yu et al. 2015). Therefore, more H₂O₂ was produced in solution with the increment of the aeration rate (Figure 7(b)). However, the DO content in the aqueous phase was limited after DO achieved saturation (Yu et al. 2015). The DO concentration measured by the multi-parameter measuring instrument (SG68 – SevenGo Duo pro, Mettler Toledo, Switzerland) remained at around 9.0 mg L⁻¹ at aeration rate 3.5 L min⁻¹, which was very close to the saturated DO at 20 °C and standard atmospheric pressure. As a consequence, a little enhancement of MO degradation efficiency and accumulated concentration of H₂O₂ are observed in Figure 7 when the aeration rate went up to 5 from 3.5 L min⁻¹.

UV–Vis absorption spectra analysis of MO

Representative UV–Vis absorption spectra changes during MO degradation by the EF system are depicted in Figure 8. It could be seen that the main absorbance spectrum at 510 nm, the characteristic absorption peak of MO.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic natural charge</th>
<th>Bond</th>
<th>Wiberg bond index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 O</td>
<td>-0.94177</td>
<td>1 O – 2 S</td>
<td>1.1804</td>
</tr>
<tr>
<td>2 S</td>
<td>2.29167</td>
<td>4 O – 2 S</td>
<td>1.2012</td>
</tr>
<tr>
<td>3 C</td>
<td>-0.18255</td>
<td>5 O – 2 S</td>
<td>1.1802</td>
</tr>
<tr>
<td>4 O</td>
<td>-0.97231</td>
<td>2 S – 3 C</td>
<td>0.7479</td>
</tr>
<tr>
<td>5 O</td>
<td>-0.94159</td>
<td>8 C – 11 N</td>
<td>1.0914</td>
</tr>
<tr>
<td>6 C</td>
<td>-0.16235</td>
<td>11 N – 12 N</td>
<td>1.4363</td>
</tr>
<tr>
<td>7 C</td>
<td>-0.20379</td>
<td>12 N – 13 C</td>
<td>1.2580</td>
</tr>
<tr>
<td>8 C</td>
<td>0.11067</td>
<td>15 C – 28 H</td>
<td>0.9161</td>
</tr>
<tr>
<td>9 C</td>
<td>-0.19437</td>
<td>17 C – 29 H</td>
<td>0.0369</td>
</tr>
<tr>
<td>10 C</td>
<td>-0.20262</td>
<td>16 C – 19 N</td>
<td>1.2217</td>
</tr>
<tr>
<td>11 N</td>
<td>-0.20549</td>
<td>19 N – 20 C</td>
<td>0.9527</td>
</tr>
<tr>
<td>12 N</td>
<td>-0.15310</td>
<td>19 N – 21 C</td>
<td>0.9534</td>
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<tr>
<td>13 C</td>
<td>0.04657</td>
<td>14 C – 15 C</td>
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<tr>
<td>14 C</td>
<td>-0.11856</td>
<td>17 C – 18 C</td>
<td>1.5685</td>
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<tr>
<td>15 C</td>
<td>-0.26238</td>
<td>20 C – 31 H</td>
<td>0.9443</td>
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<tr>
<td>16 C</td>
<td>0.23915</td>
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<td>0.9319</td>
</tr>
<tr>
<td>17 C</td>
<td>-0.23410</td>
<td>20 C – 33 H</td>
<td>0.9319</td>
</tr>
<tr>
<td>18 C</td>
<td>-0.18059</td>
<td>21 C – 34 H</td>
<td>0.9348</td>
</tr>
<tr>
<td>19 N</td>
<td>-0.43123</td>
<td>21 C – 35 H</td>
<td>0.9325</td>
</tr>
<tr>
<td>20 C</td>
<td>-0.35940</td>
<td>21 C – 36 H</td>
<td>0.9325</td>
</tr>
<tr>
<td>21 C</td>
<td>-0.35997</td>
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<td></td>
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</table>
corresponding to the azo form, dramatically decreased with the reaction time, indicating a rapid decomposition process of the MO molecules. Although there existed an efficient degradation process of the MO, only a TOC removal of 32% was acquired during 90 min. Meanwhile, two weak absorption peaks at 270 nm and 320 nm, attributed to the existence of aromatic rings, did not obviously decrease in intensity, which suggested MO was incompletely mineralized and further decomposed to produce many intermediates of substituted benzene (Zhao et al. 2011; Zugle & Nyokong 2013; Arab Chamjangali et al. 2015; Zhiyong et al. 2014).

Identification of intermediates and proposed degradation pathway of MO

Optimization and calculation result analysis

The natural bond orbital (NBO) analysis method was performed on the analysis of structure geometry and interaction among bonds of organic molecules (Nori-Shargh et al. 2011; Xin et al. 2015; Savithiri et al. 2016). This study introduced the calculation method of quantum chemistry, for the MO molecule, NBO analysis was performed on space structure geometry optimization and space charge distribution at B3LYP/6-311G (d, p) level by Gaussian 09 software. The optimized conformation of MO is shown in Figure 9 and the atomic natural charge and Wiberg bond index of MO are shown in Table 1. As can be seen from Table 1, on the one hand, O on the sulfo group with the largest negative charge was the most liable to be attacked by electrophilic -OH. N on the azo-group, N and C on the dimethylamino with higher negative charge were also relatively vulnerable to attack by -OH. On the other hand, 17C – 29H on the benzene ring was the weakest site, prone to have the bond broken, then, the C–S bond. In addition, C–N bonds were always the weaker sites and were easily cleaved from the benzene ring, while C–C bonds on the benzene ring were hard to break.

<table>
<thead>
<tr>
<th>Compound list</th>
<th>Molecular formula</th>
<th>Structure</th>
<th>$R_t$ (min)</th>
<th>Molecular ions (m/z)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>C$<em>{14}$H$</em>{13}$N$_3$SO$_3$</td>
<td><img src="image1" alt="Structure" /></td>
<td>15.428</td>
<td>304.9 ([M-H]$^-$)</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>{14}$H$</em>{13}$N$_3$SO$_5$</td>
<td><img src="image2" alt="Structure" /></td>
<td>4.261</td>
<td>334.4 ([M-H]$^-$)</td>
</tr>
<tr>
<td>3</td>
<td>C$<em>{14}$H$</em>{11}$N$_3$SO$_8$</td>
<td><img src="image3" alt="Structure" /></td>
<td>4.261</td>
<td>380.7 ([M-H]$^-$)</td>
</tr>
<tr>
<td>4</td>
<td>C$<em>{14}$H$</em>{16}$N$_3$O</td>
<td><img src="image4" alt="Structure" /></td>
<td>15.428</td>
<td>240.7 ([M-H]$^-$)</td>
</tr>
<tr>
<td>5</td>
<td>C$<em>{14}$H$</em>{14}$N$_3$O$_2$</td>
<td><img src="image5" alt="Structure" /></td>
<td>4.915</td>
<td>255 ([M-H]$^-$)</td>
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<tr>
<td>6</td>
<td>C$<em>{6}$H$</em>{6}$NSO$_3$</td>
<td><img src="image6" alt="Structure" /></td>
<td>8.647</td>
<td>171.9 ([M]$^-$)</td>
</tr>
<tr>
<td>8</td>
<td>C$<em>{6}$H$</em>{6}$SO$_3$</td>
<td><img src="image7" alt="Structure" /></td>
<td>4.915</td>
<td>154.8 ([M-H]$^-$)</td>
</tr>
<tr>
<td>10</td>
<td>C$<em>{6}$H$</em>{6}$SO$_4$</td>
<td><img src="image8" alt="Structure" /></td>
<td>14.347</td>
<td>172.9 ([M]$^-$)</td>
</tr>
<tr>
<td>11</td>
<td>C$<em>{6}$H$</em>{6}$SO$_4$</td>
<td><img src="image9" alt="Structure" /></td>
<td>7.784</td>
<td>189.9 ([M-H]$^-$)</td>
</tr>
</tbody>
</table>

Identification of intermediates and degradation mechanism for MO

In an attempt to identify the MO degradation products, MO solution obtained after 60 min oxidation was further measured using LC-MS, taking into account the above calculation result analysis, the nine main intermediates of MO are described in Table 2, for which LC-MS spectra are shown in Figures S1–S5 (available with the online version of this paper). The identification of the possible degradation pathways and reaction
routes is depicted in Figure 10. The possible degradation mechanism of MO mainly involved four degradation patterns. First and foremost, under the acidic aqueous solution conditions, the acid sulfo and two intramolecular alkaline dimethylamino on MO forming the inner salt type of the two dimethylamino phenyl azobenzene sulfonate, namely compound 1, containing a para-quinone conjugate system. Route a indicated that the methyl group of compound 1 was attacked by -OH to oxidation, resulting in the formation of intermediate 2, followed by successive oxidation of methyl and substitution of quinone to form compound 3 (Baiocchi et al. 2002). Route b was initiated by -OH acting on the C – S bonds of the sulfophenyl group to form intermediate 4, and further oxidation producing intermediate 5. Route c and d were the main degradation mechanism for MO; the oxidation of compound 1 by -OH led to the cleavage of the –N=N–groups and C–N bonds, with the consequent loss of decolorization (Baiocchi et al. 2002; Nerenokte & Yilmaz 2008; Gupta & Pal 2014). Followed by substitution, intermediates 6 and 8 were produced in route c and d to form intermediate 10, then intermediate 10 attacked by -OH might be converted to intermediate 11 during further degradation.

CONCLUSIONS

Magnetic Fe₃O₄ nanoparticles were synthesized effectively and used as a heterogeneous catalyst to degrade MO from aqueous solution in the EF process. Operating parameters such as current density, pH, catalyst dosage and aeration rate all strongly affected the MO degradation efficiency. Higher current density and aeration rate facilitated the degradation of MO. The EF process did not require a high dosage of Fe₃O₄ MNPs and could work over a wide pH range (2–9.5), although better results were attained under acidic conditions. Furthermore, the accumulated concentration of H₂O₂ and the concentration of iron leaching were determined under different operating conditions. The result testified that various parameters exerted a vital influence on the performance of degradation efficiency according to changes of the concentration of H₂O₂ and iron leaching. The results obtained from the change of UV-Vis absorption spectra and TOC indicated that the intermediates were quite refractory to further mineralization, resulting in ineffective mineralization. Finally,
possible degradation pathways of MO were speculated on the basis of the NBO analysis method and nine intermediates were identified by LC-MS. The main degradation mechanism of MO by the EF system involved a series of processes, such as bond breaking, substitution and hydroxylation, etc.

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