Degradation of Reactive Brilliant Red X-3B by zero-valent iron/activated carbon system in the presence of microwave irradiation
Fei Pan, Yin Luo, Li-Rong Zhang and Jie Fu

ABSTRACT
Reactive Brilliant Red X-3B in aqueous solution could be degraded rapidly by zero-valent iron/activated carbon in the presence of microwave irradiation (ZVI/AC/MW). From the analysis of ultraviolet-visible adsorption, chemical oxygen demand, total organic carbon, infrared spectra and capillary electrophoresis, we found the degradation was complete and no intermediates remained in the final solution treated for 2 min. Considering the many advantages including high degradation ratios, short reaction time, low costs, no intermediates and no secondary pollution, this method might be fit for dealing with various azo dye wastewaters on a large scale.

Key words | activated carbon, degradation, microwave, Reactive Brilliant Red X-3B, zero-valent iron

ABBREVIATIONS
AC activated carbon
AR% absorbance removal percentage
CAP characteristic absorption peaks
CE capillary electrophoresis
COD chemical oxygen demand
CODR% chemical oxygen demand reduction percentage
IR infrared
MW microwave
PDA photo diode array
SDS sodium dodecyl sulfate
TOC total organic carbon
TOCR% total organic carbon removal percentage
UV–Vis ultraviolet-visible
X-3B Reactive Brilliant Red X-3B
ZVI zero-valent iron

INTRODUCTION
Synthetic dyes are widely used in many industries, such as textile, cosmetic, printing, drug, and food processing (Fu et al. 2010). These dyes constitute one of the largest groups of organic compounds that represent an increasing environmental danger (Ai et al. 2008). About a half of global production of synthetic textile dyes is classified into azo compounds that have the \(-\text{N} = \text{N}\)- chromophore in their molecular structure (Liu et al. 2007). Azo dyes are very difficult to be treated in environmental systems, because the sulfonic acid groups within their chemical structure make them very water-soluble and polar (Bauer et al. 1999; Stylidi et al. 2004; Zhang et al. 2007). Different technologies have been studied for the degradation of azo dyes in wastewater, such as biodegradation (Manu & Chaudhari 2003), ultrasound irradiation (Li et al. 2008), photocatalytic process (Zeng et al. 2009), coagulation (Sarasa et al. 1998), and electrochemical oxidation (Rajkumar & Kim 2006). Nevertheless, these methods were insufficient to treat azo dye wastewater in high concentration and color.

During the past three decades, zero-valent iron (ZVI) has been shown to be one of efficient materials in water/wastewater technologies (Shen et al. 2007; Liu et al. 2007; Noubactep et al. 2010; Le et al. 2011). ZVI has a rich source and could be obtained from industrial wastes. The solid form of ZVI especially makes it conventional to be applied in the engineering. Moreover, when combined with different materials, it can trigger synergy effect involving multiplex mechanisms such as adsorption,
coprecipitation, internal electrolysis, reduction and oxidation. ZVI/AC system was a promising method to degrade organic compounds by means of internal electrolysis (Shen et al. 2001; Liu et al. 2007). Recently, the MW technique has also found applications in environmental engineering with the capability of induced oxidation and assisted adsorption (Ai et al. 2008). However, the combination of ZVI/AC and MW to treat dye wastewater has hardly been reported. Therefore, in this paper, we have investigated the degradation of a commonly used azo dye, X-3B (Figure 1), by the synergistic effect of ZVI/AC in the presence of MW irradiation. We anticipate that this result would be helpful for researchers attempting to find cost-effective methods to treat azo dye wastewater.

METHODS

Materials

Commercial dye X-3B was obtained from Jiangsu Chemicals Company (Jiangsu, China) and used without further purification. Other chemicals used in the experiment were of analytical grade. Distilled water was used throughout the whole experimental process.

ZVI (iron chippings) was obtained from Wuhan Air Compressor Co., Ltd. (China). The ZVI was washed by industrial alkali to remove oil stain, and then soaked and activated in HCl (1 M, 20 min) (Li et al. 1999). This was followed by several washings with distilled water and filtrations to remove the excess HCl. The ZVI was then dried in an oven at 120°C for approximately 3 h. The dried ZVI was crushed in a mortar until the sample was classified according to particle size by a mesh analysis.

AC of particle size 8–12 mesh was obtained from Tangshan Huaneng Technology Carbon Co., Ltd (China). In order to avoid the influence of carbon black and other impurities, the AC was washed in distilled water for 4 h and then dried in an oven at 120°C for approximately 3 h.

Procedure

150 mL X-3B solution (1 g/L) was placed in a quartz reactor (500 mL) and 50 g mixture of ZVI and AC (1:1, v/v) was added. The mixture was irradiated in a G90T23ASP-2B microwave oven (800 W, Guangdong Galanz Group Co., Ltd., China) for 2 min, and then filtered. A comparative study of X-3B solution by ZVI/AC without MW irradiation was performed in a controlled procedure over a reaction time of 2 h.

Analysis

Analysis by UV–Vis absorbance

A UV–Vis absorption spectrum of X-3B, measured on a UV1100 spectrophotometer (Beijing Rayleigh analytical instrument Corp., Beijing, China), is shown (Figure 2). Absorbance peaks (231 and 285 nm) in the UV range were the CAPs of the benzene ring while 329 nm was the CAP of naphthalene ring and 512 and 540 nm in the Vis range were the CAPs of conjugated chromophoric system, which was formed by –N=N– unit, benzene ring and naphthalene ring. In this study, we monitored changes in the analytical wavelengths (231, 329 and 540 nm) as indicative to the degradation of benzene ring, naphthalene ring, and conjugated –N=N– chromophoric system, respectively. The AR% of CAP was calculated [Equation (1)]:

\[
AR\% = \frac{A_0 - A_t}{A_0} \times 100
\]

Figure 1 | Chemical structure of X-3B.

Figure 2 | UV–Vis absorption spectrum of X-3B.
where $A_0$ was the absorbance value of the initial X-3B solution at CAP (Abs), and $A_t$ the absorbance value of the X-3B solution after $t$ min at CAP (Abs).

**Analysis of COD reduction**

COD was measured on a JH-12 COD analysis apparatus (Qingdao Laoshan electron instrument Corp., Qingdao, China) and COD reduction percentage (CODR%) were calculated [Equation (2)]:

$$\text{CODR\%} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$$

where COD$_0$ was the COD value of the initial X-3B solution (mg/L), and COD$_t$ the COD value of the X-3B solution after $t$ min (mg/L).

**Analysis of TOC**

A Multi N/C TOC Analyzer (Carl Zeiss Yena, Germany) was used to measure TOC concentration according to National Environmental Protection Agency (1991), for which the standard is GB13193-91. All samples were diluted 10 times before analysis. The TOC removal percentage (TOCR%) was calculated [Equation (3)]:

$$\text{TOCR\%} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100$$

where TOC$_0$ was the value of the solution that was not treated and TOC$_t$ was the value of the solution after $t$ min.

**Analysis of CE**

Samples were analysed on a Beckman P/ACE™ MDQ CE apparatus. The temperature of the capillary and the samples was maintained at 25°C. Detection was performed at 196 nm with 10 nm band width by a PDA detector. The buffer consisted of 20 mM SDS, 5 mM Na$_2$B$_4$O$_7$ and 3 mM Na$_3$PO$_4$. Samples were pressure-injected at the anodic side at 0.5 Psi for 5 s. A constant voltage (20.0 kV) was used for all the experiments.

**Results and Discussion**

**Degradation efficiency**

The removal percentages of color, COD, and TOC of ZVI/AC and ZVI/AC/MW approaches are shown (Table 1). With the ZVI/AC process, after internal electrolysis for 2 h, the A$_{231}$% and A$_{329}$% were up to approximately 76% and 87% and A$_{540}$% reached approximately 97%. This suggested that the conjugated chromophoric system was firstly degraded, and then benzene ring and naphthalene ring began to be degraded with the degradation of the latter appearing the easiest. However, the CODR% and TOCR% values of ZVI/AC were equal or less than 50%, indicating that the mineralization was not complete and many organics still existed in the solution.

Compared to the long contact time of ZVI/AC, ZVI/AC/MW showed a distinct advantage. After treating for 2 min, all the AR% were greater than 90%, and CODR% and TOCR% were around 80%. This suggested that most of the dye molecules were cleaved and degraded, and the mineralization was greatly improved. During the process, it was clear that MW played a key role.

In the MW irradiation, an arc was produced between ZVI particles and the temperature rapidly increased to form ‘hot spots’ (Figure 3). Because of the thorough mixing of ZVI and AC, the temperature of the AC around these ‘hot spots’ would rapidly increase up to 1,200°C and

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<th>Table 1</th>
<th>AR%, CODR% and TOCR% of ZVI/AC and ZVI/AC/MW approaches</th>
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<td>A$_{540}$R%</td>
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<tr>
<td>ZVI/AC</td>
<td>97.30 ± 1.24$^a$</td>
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<tr>
<td>ZVI/AC/MW</td>
<td>93.04 ± 4.82</td>
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$^a$Each value was the mean ± S.D. ($n$ = 3).
since the inner pores of AC would be quickly extended (Liu et al. 2004; Senthilkumar et al. 2006), the adsorption of AC would be enhanced. In addition, the ZVI promoted the degradation of adsorbed dye molecules and the ‘strike fire’ in the MW field became more violent. Large amount of plasmas (such as Fe²⁺ and Fe³⁺), strong oxidants (such as O₃ and •OH) and arc (UV) were produced, which would degrade the adsorbed dye molecules either on the surface of ZVI and AC or in the pores of AC.

Both ZVI and AC surface structures significantly changed before and after MW irradiation (Figure 4). The surface of ZVI became irregular and proliferated with a honeycomb of holes while on the surface of AC, both the micropore size and number increased, and the shape became irregular.

The effect of particle size of ZVI

ZVI with different particle sizes were used to investigate the effect of the particle size and the results were summarized in Table 2. As shown in Table 2, the optimal particle size of ZVI was 0.9–2 mm, and below or above this size would decrease the degradation efficiency. In theory, the smaller particle sizes were favorable and could form more microbatteries. However, in fact, the smaller particles easily caked and settled which reduced the contact areas with wastewater. Therefore, we used 0.9–2 mm ZVI in the experiment.

The effect of pH value

The actual dye wastewater has a wide range of initial pH values, and the X-3B solution pH is an important parameter affecting the kinetics in the reduction process by

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<th>Particle sizes of ZVI (mm)</th>
<th>AR%</th>
<th>CODR%</th>
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<tr>
<td>&gt;2</td>
<td>92.56</td>
<td>49.03</td>
</tr>
<tr>
<td>0.9–2</td>
<td>99.60</td>
<td>64.54</td>
</tr>
<tr>
<td>0.45–0.9</td>
<td>98.38</td>
<td>46.16</td>
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<tr>
<td>0.125–0.45</td>
<td>97.10</td>
<td>42.86</td>
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Figure 4 | SEM photographs of surface of ZVI and AC before and after MW irradiation: (a) AC, before MW irradiation, (b) AC, after MW irradiation, (c) ZVI, before MW irradiation and (d) ZVI, after MW irradiation.
ZVI (Huang et al. 1998). Figure 5 illustrated the AR% and CODR% at different initial pH values. As shown in Figure 5, lower pH level was favorable for higher AR% and CODR%. With increment in pH value, the AR% and CODR% values gradually decreased.

The main reaction of ZVI in solutions with different pH values are presented as following equations:

\[
\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-
\]

(4)

\[
\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2
\]

(5)

According to Nernst Equation, the reduction potential for Fe\(^{2+}\)/Fe increases with an increase of the H\(^+\) concentration and thus low pH level promoted the reduction of azo dye. The result was consistent with that from Cao et al. (1999) and Liu et al. (2007). However, neutral condition was favorable in persulfate/ZVI system (Le et al. 2011).

The effect of initial dye concentration

The effect of initial X-3B concentration on AR% and CODR% was shown in Figure 6. Different initial X-3B concentrations resulted in different AR% and CODR% values. AR% and CODR% decreased with increasing dye concentration. And when the dye concentration was higher than 2 g/L, the AR% and CODR% values decreased below 90 and 50%, respectively. Thus the applicable dye concentration in the ZVI/AC process should not be higher than 2 g/L. The possible reason was that the adsorption ability and internal electrolysis approached saturation gradually with the increase of initial dye concentration.

Degradation products

Samples obtained from the final solution treated by ZVI/AC and ZVI/AC/MW were dried at 60 °C and the IR spectra performed on the residual solid (Figure 7). Figure 7(a) was the IR spectrum of X-3B. 1,500–1,600 cm\(^{-1}\) was the absorption of naphthalene ring and triazine ring and 1,000–1,200 cm\(^{-1}\) was the absorption of sulfonate radical. The absorption of –N=N– at 2,000–2,500 cm\(^{-1}\) was very weak.
and not readily observed in the experiment. The absorption of ZVI/AC degradation products (Figure 7(b)) showed very little change in absorption peaks, reflecting minimal change in structure of the dye and suggesting that the dye molecules were not degraded. However, as shown in IR spectrum of ZVI/AC degradation products (Figure 7(c)), the absorption peaks at 1,500–1,600 cm\(^{-1}\) disappeared, indicating that the aromatic and triazine rings had been opened and degraded. The absorption peaks at 1,000–1,200 cm\(^{-1}\) were significantly decreased with the only remaining strong absorption band at around 1,100 cm\(^{-1}\) being that of the IR absorption of sulfate. The BaCl\(_2\) test also demonstrated the existence of sulphate. This suggested that sulfonate was cleaved from naphthalene ring and oxidized to sulfate. By comparing Figure 7(a) and (c), it was clear that the structure of the dye after ZVI/AC/MW was significantly changed and most organics were mineralized.

The analysis of CE was in agreement with the IR spectra. As shown in Figure 8(a), the peak at approximately 5.2 min presented aniline and the one at approximately 13.2 min presented X-3B. It was clear that aniline, which was the main intermediate in the internal electrolysis of azo dyes (Figure 9), and X-3B were detected in the degradation products of ZVI/AC (Figure 8(c)). However, there were no peaks in the degradation products of ZVI/AC/MW (Figure 8(d)), suggesting the mineralization of ZVI/AC/MW was greatly improved.

**CONCLUSIONS**

ZVI/AC/MW had higher degradation efficiency than ZVI/AC when treating X-3B. The mineralization of ZVI/AC/MW was more complete and no intermediates were retained. In addition, the MW irradiation time was much shorter than the internal electrolysis. Considering these advantages, this method might be broadly extended in the treatment of textile dye wastewater.

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**REFERENCES**


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