Heterogeneous photo-catalysis system for the degradation of azo dye Reactive Black 5 (RB5)

Yao-Hui Huang, Hau-Cheng Wei and Hung-Ta Chen

Abstract
This study investigated a heterogeneous photo-catalysis system by introducing a novel brick supported iron oxide (denoted as B1) for the heterogeneous photoassisted degradation of Reactive Black 5 (RB5) at pH value from 3 to 7 in a three-phase (gas–liquid–solid) fluidized bed reactor (3P-FBR). Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD) and N2 adsorption/desorption were used to characterize the B1 catalyst. The in situ formation of hydrogen peroxide and the depletion of oxalic acid by photochemical cycle of Fe(III)-oxalate complex under UVA light (λ = 365 nm) were studied. The effects of the solution pH and the concentration of oxalic acid on the degradation of RB5 are elucidated. About 90% decolourization was measured and 80% of the total organic carbon (TOC) was eliminated at pH 5.0 after 120 min for 20 mg/L RB5 in presence of 10 g/L B1 catalyst, 30 mg/L oxalic acid under 15 W UVA light. A mechanism for the photocatalytic degradation of RB5 over B1 catalyst is proposed.

Key words | decolourization, iron oxide, oxalic acid, Reactive Black 5, total organic carbon

Introduction
RB5 is one of the oldest reactive dyes and is used very heavily in textile dyeing. Dye effluents, discharged from the printing, dyeing and textile industries, may contain chemicals that exhibit toxic effects toward microbial populations and can be toxic and/or carcinogenic to mammals. From the environmental point of view, particularly the removal of synthetic dyes is of great concern, as they or their degradation products might be of toxic nature and consequently their treatment cannot depend on biodegradation alone (Arslan & Balcioglu 1999). Accordingly, the degradation of dye house effluents has become a critical step in treating textile wastewater. Conventional methods including physical, chemical and biological processes were used to remove dyes in the effluent. Unfortunately, most azo dye compounds are resistant to bacterial activity and biological treatment alone will take a long time to be effective. Therefore, alternative technology must be developed to help solve the problem.

Advanced oxidation processes (AOPs) are remediation processes that produce the highly reactive hydroxyl radical (OH) to degrade organic pollutants. Since the 1990s, AOPs have attracted considerable attention in relation to wastewater treatment (Bahorsky 1997; Fernandez et al. 1999; Lee & Hosomi 2001). Among AOPs, one of the most important processes used to generate hydroxyl radical (OH) is Fe2+/H2O2/UV system, in which the catalyst of ferrous ions is dissolved in water, so it is called the homogeneous photo-Fenton process. In this system, Fe2+ in solution acts as a homogeneous catalyst. However, the homogeneous photo-Fenton process has a marked shortcoming. It produces iron-containing waste sludge whose disposal is difficult and expensive. This disadvantage limits the further application of the homogeneous photo-Fenton process in treating wastewater. Therefore, the heterogeneous photo-Fenton or photo-Fenton-like processes have been developed by coating Fe ions in iron oxide onto porous solid as a catalyst. It is called a heterogeneous catalyst because it does not dissolve in water (Hsueh et al. 2006a; Huang et al. 2009 a, b; Huang & Huang 2009).

In our previous study, one kind of grained iron oxide (the inner support is activated alumina) has successfully been used as heterogeneous catalyst for degradation of azo dye at neutral pH value, and the thermodynamics and kinetics of the adsorption of azo dye onto the iron oxide have been studied as well (Hsueh et al. 2006a, b). Furthermore, iron oxide can be also applied as adsorbent to treat heavy

In AOPs, oxalic acid is usually the reason for the residual total organic carbon (TOC). However, the depletion of oxalic acid by photochemical/chemical cycling of Fe(III)/Fe(II)-oxalate complexes under sunlight has been fully studied. Some references have indicated that the mechanism of the photo-induced Fe(III) reduction is assisted by oxalic acid and thus enhances the generation of \( \cdot \text{OH} \) for the degradation of organic pollutants (Duesterberg et al. 2005; Jeong & Yoon 2004; Zazo et al. 2005). It has been also found that \( \text{H}_2\text{O}_2 \) can be produced via the reduction of oxygen with intermediates formed from photolysis of Fe(III)-oxalate complexes (Sedlak & Hoigne 1993). Therefore, oxalic acid can be regarded as the oxidizer instead of \( \text{H}_2\text{O}_2 \) in photo-Fenton or photo-Fenton-like reaction.

The purpose of this study is to examine the degradation of azo dye RB5 in irradiated, aerated suspensions containing the B1 catalyst and oxalic acid. Moreover, the mechanism for photocatalytic degradation of B1 catalyst–oxalate complexes is also proposed.

MATERIALS AND METHODS

Materials

RB5, \( \text{C}_{26}\text{H}_{21}\text{N}_{5}\text{Na}_4\text{O}_{19}\text{S}_6 \), was purchased from Aldrich Chemical Company (Amherst, NY, USA); it was 55% pure, and had a molecular weight of 991.82. The structure of RB5 is presented below (Figure 1). Oxalic acid (J. T. Baker) was of analytical reagent grade and was used without further purification. The B1 catalyst, iron oxide on a brick grain support, was prepared in the following manner. Deionized and doubly distilled water were used throughout this investigation.

Characterization of the B1 catalyst

The sizes of the brick grain support particles and the B1 catalyst particles were obtained using a JEOL JSM-6700F scanning electron microscope (SEM). The atomic composition of the B1 catalyst surface was elucidated by energy dispersive spectrometer (EDS) using an OXFORD INCA-400 spectrometer. B1 was characterized using a powder diffractometer (Rigaku RX III) with Cu K radiation. The accelerating voltage and current were 40 kV and 30 mA. The specific surface area of B1 was measured by the BET method. The TOC was analysed using a SIEVERS 900 analyser.

Experimental set-up

The experimental set-up used to determine the removal efficiency of RB5 in the 3P-FBR at room temperature is shown in Figure 2. The irradiation source was a 15 W UVA lamp (\( \lambda = 365 \text{ nm} \)) fixed inside a cylindrical Pyrex tube (allowing the wavelengths 320 nm to pass). The total volume of the solution was 1 L, the initial concentration of RB5 was 20 mg/L (except as otherwise specified) and a predetermined quantity of potassium nitrate (250 mg/L, for ionic strength control) and oxalic acid (0, 10, 20, 30 and 50 mg/L) was added into the reactor.

RESULTS AND DISCUSSION

Characterization of the B1 catalyst

Figure 3 presents SEM micrographs of the brick grain support and the B1 catalyst. Figure 3(a) (1,000×) indicates
that the original brick grain support is irregularly shaped. It was smoother after the reaction in the FBR had proceeded for 3 months, as displayed in Figure 3(b) (1000×). Table 1 presents the quantitative surface chemical compositions of the B1 catalyst, determined by EDS.

Figure 4 depicts the X-ray diffraction (XRD) patterns of the brick grain support and B1 catalyst using Joint Committee on Powder Diffraction Standards (JCPDS) diffraction files. The main diffraction peaks of the brick grain support (Figure 4(a)) at 2θ = 20.86°, 26.64° and 50.14° were carefully compared with the standard for silica (SiO2-file number 46-1045). Accordingly, the XRD analysis demonstrated that the surface of the B1 catalyst is amorphous.

Degradation of RB5 under dissolved oxygen condition

The following experiments were undertaken at pH 5 to evaluate the photo-catalytic activity of the B1 catalyst (Figure 5), and all the parameters are shown in Table 2. Without catalyst and oxalic acid but with only 15 W UVA

**Table 1** | Surface atomic composition of support and B1 catalyst by EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>Support (at %)</th>
<th>B1 catalyst (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>17.82</td>
<td>33.59</td>
</tr>
<tr>
<td>O</td>
<td>52.73</td>
<td>43.50</td>
</tr>
<tr>
<td>Fe</td>
<td>3.96</td>
<td>19.44</td>
</tr>
<tr>
<td>Al</td>
<td>8.95</td>
<td>1.74</td>
</tr>
<tr>
<td>Si</td>
<td>16.54</td>
<td>1.73</td>
</tr>
</tbody>
</table>
(curve a), the RB5 concentration barely declined, indicating that the degradation of RB5 by photolysis is limited. Without UVA light but with 10 g/L B1 catalyst and 30 mg/L oxalic acid (curve b), the RB5 concentration decreases approximately 10% during 120 min of reaction, perhaps because of the adsorption effect. Without catalyst but with 15 W UVA light and 30 mg/L oxalic acid (curve c), the degradation of RB5 is very limited (about 20%). Oxidation by oxalyl radical anion (\( \text{C}_2\text{O}_4^- \)) and carbon dioxide radical anion (\( \text{CO}_2^- \)), which were generated by the direct photolysis of oxalic acid under UVA light, may have been accountable for the degradation of RB5. Without UVA light and oxalic acid but with only 10 g/L B1 catalyst (curve d), the RB5 concentration decreases about 60% during 120 min of reaction. Without oxalic acid but with 15 W UVA light and 10 g/L B1 catalyst (curve e), the RB5 concentration dropped rapidly initially and then slowly reached 65%. The degradation of RB5 is most rapid in the presence of 15 W UVA light, 10 g/L B1 catalyst and 0.33 mM oxalic acid (curve f); the decrease of RB5 was close to 90% after 120 min.

The decrease of RB5 may result from not only the degradation but also the adsorption by B1 catalyst; therefore, the experiments of desorption must be done to show the fact. The desorption was carried out at pH 11.5 after 120 min reaction. It is easily discovered that the final RB5 concentrations at 160 min of curves b, d and e are ca. 97% of the initial RB5 concentrations, which means the decrease of RB5 is due to the adsorption, not the degradation. However, curve f shows a different result and indicates that there is only less RB5 desorbed from the B1 catalyst. The reason is that the carbon dioxide radical anion (\( \text{CO}_2^- \)) reacts with oxygen (when present) to yield the superoxide radical anion (\( \text{O}_2^- \)) and then the formation of Fe\(^{2+} \) by UVA light on the surface of the catalyst generates hydroxyl radical (\( \cdot \text{OH} \)) by decomposing \( \text{H}_2\text{O}_2 \), promoting the degradation of RB5.

### Effect of the solution pH

Degradation of RB5 was photoassisted at pH values from 3 to 7 in the catalyst/oxalic acid system (Figure 6). Clearly, the reaction occurred over a wide range of pH values from acidic to neutral, unlike in the Fenton system (pH \( \sim 3 \)). Figure 6 reveals that the degradation rate decreases with increasing initial solution pH. About 1.65 mg/L ferrous ions were detected during the reaction by atomic absorbance spectrophotometer in this system. The RB5 concentration decreases because of adsorption at pH 6–7 (at neutral pH). On the contrary, the efficiency of the RB5 degradation at low pH value (3–5) is more than at high pH value (6–7). The adsorption of RB5 by the B1 catalyst should also be considered. In the pH range of 3 to 5, it is obviously found that less RB5 was desorbed, no more than 5% of the initial RB5 concentration. This proves that the removal of RB5 was due to degradation, not adsorption.

### Effect of oxalic acid concentration

Photolysis of the ferrioxalate complex is followed by dissociation of oxalyl radical anion (\( \text{C}_2\text{O}_4^- \)) from the surface and detachment of the reduced surface iron centre from the crystal lattice and transfer into solution. The oxalate radical reacts with dissolved oxygen, yielding the superoxide radical anion (\( \text{O}_2^- \)), which further reacts with Fe\(^{2+} \) to form hydrogen peroxide. The hydrogen peroxide undergoes the Fenton reaction to yield hydroxyl radical (\( \cdot \text{OH} \)). Figure 7 plots the RB5 concentration against reaction time (0–120 min) for various concentrations of oxalic acid. The degradation of RB5 increases with increasing concentration from 10 to 50 mg/L, because more hydroxyl radical (\( \cdot \text{OH} \))...
Mineralization of RB5

Reaction intermediates are known sometimes to be formed by the oxidation of organic dyes and some may be longer-lived and even more toxic to aquatic animals and human beings than parent compounds. Although identifying the intermediates is very important in determining the reaction path of the photoassisted degradation of RB5, this investigation more strongly focuses on the extent of mineralization of RB5 with reference to practical industrial applications. Although alternative techniques for evaluating the extent of mineralization of organic pollutants may be available, the removal of TOC is commonly used in the industrial treatment of wastewater to determine this extent of mineralization. Therefore, this study focuses on the removal of TOC from RB5 solution, rather than on identifying reaction intermediates.

Figure 8 plots the TOC of 20 mg/L RB5 against time (0–120 min) under the conditions of 50 mg/L oxalic acid, 10 g/L B1 catalyst and 15 W UVA light. The TOC decreases during the first 20 min because of the adsorption of RB5 on the surface of the B1 catalyst. Between 15 and 120 min, the decrease in TOC indicated the ferrioxalate species are generated by UVA light on the surface of the B1 catalyst and that these generate hydroxyl radical (OH) by the decomposition of oxalic acid. This result clearly reveals that the presence of UVA light effectively promotes the mineralization of RB5.
Mechanism of RB5 degradation

Based on the above results, the following simple mechanism for this system under dissolved oxygen is presented. Scheme 1 shows the various surfaces of the catalyst and solution reaction, and the intermediates and products are via the photolysis of Fe(III)-oxalate and Fe(III)-RB5 in heterogeneous photoassisted Fenton systems. It can be also seen that the complexes of oxalate (C₂O₄²⁻) can transform to oxalyl radical anion (C₂O₄⁻) under irradiation. The oxalyl radical anion (C₂O₄⁻) reacts with molecular oxygen to give CO₂ and superoxide radical anion (O₂⁻). Hydrogen peroxide formed from O₂⁻/HO₂⁻ is another significant oxidant of Fe (II) by the Fenton reaction to yield hydroxyl radical (•OH), which degraded the RB5 dye.

CONCLUSIONS

This investigation proposes a novel catalyst under oxalic acid and dissolved oxygen to degrade the azo dye RB5. The catalyst greatly promotes not only the decolourization but also the mineralization of RB5. About 90% decolourization was measured and 80% of the total organic carbon was eliminated at pH 5 after 120 min in presence of 20 mg/L RB5, 10 g/L B1 catalyst, 30 mg/L oxalic acid under 15 W UVA light. A simple mechanism by which the heterogeneous catalyst decolours and mineralizes RB5 is presented, based on experimental results. Therefore, the B1 catalyst has potential as a heterogeneous catalyst of photoassisted degradation of organic compounds and has the advantage of prevention of iron sludge generation compared with the traditional homogeneous Fenton reaction.

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REFERENCES

References are omitted for brevity, but they can be found in the original text.