Photoassisted Degradation of Azodyes over FeO\textsubscript{x}H\textsubscript{2x−3}/Fe\textsuperscript{0} in the Presence of H\textsubscript{2}O\textsubscript{2} at Neutral pH Values

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Fe\textsuperscript{0} was calcined in air at 200 °C and showed enhanced activity in three cycling runs for the degradation of acid red B (ARB) in the presence of H\textsubscript{2}O\textsubscript{2} under UVA irradiation. Subsequently, the catalyst’s activity was maintained effectively after 10 successive cycling experiments. Moreover, the catalyst was found to be highly effective for the degradation of nonbiodegradable azodyes ARB, reactive brilliant red X-3B, reactive red K-2G, cationic red X-GRL, and cationic blue X-GRL at neutral pH values. On the basis of characterization by X-ray diffraction, X-ray photoelectron spectroscopy, and Fourier transform infrared spectra, the surface layer of the catalyst was mainly composed of α-FeOOH and γ-Fe\textsubscript{2}O\textsubscript{3}, and the core was Fe\textsuperscript{0} (FeO\textsubscript{x}H\textsubscript{2x−y}/Fe\textsuperscript{0}). FeO\textsubscript{x}H\textsubscript{2x−3}/Fe\textsuperscript{0} was very easily recovered from the reaction system by magnetic separation. The degradation of azodyes came from the synergistic effect of the catalysis of galvanic cells and the oxidation of heterogeneous photo-Fenton reaction on the basis of all information obtained under different experimental conditions. By the total organic carbon and GC–MS analysis, the degradation process of ARB was shown to proceed with decolorization and naphthalene ring openings into CO\textsubscript{2} and small organic acids.

Introduction

Industrial wastewater is becoming more and more complex with the increasing diversity of industrial products. Textile and dyestuff industries produce large amounts of wastewater containing various dye pollutants. Of the dyes available on the market today, azodyes represent approximately 50−70% (1). Previous research suggests that most azodyes are nonbiodegradable and their release into the environment poses a major threat to the surrounding ecosystems (2). The development of Fenton-immobilized catalysts has been considered as a cost-effective alternative as pretreatment of biological treatment processes for the abatement of dye-containing wastewater (3).

Since iron is relatively inexpensive and nontoxic, it has been widely used in different environmental treatment processes. For example, utilization of Fe\textsuperscript{0} as a chemical reductant to remove pollutants in water has been intensively investigated (4, 5). Moreover, Waite (6) and Cheng (7) have reported that molinate and phenol can be oxidized by reactive oxygen species generated from the reaction of Fe\textsuperscript{0} and oxygen. Additionally, Fe\textsuperscript{0} has been studied as a precursor of Fe\textsuperscript{3+} in Fenton reactions in acid media (2, 6). The use of Fe\textsuperscript{0} instead of iron salts has three advantages: the concentration of iron ions in solution after the treatment is significantly lowered (2, 9); the additional loading of treated wastewater with other anions (Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}) is avoided (2); and the remaining Fe\textsuperscript{0} can be easily recovered from the solution (2). However, the direct electron transfer from Fe\textsuperscript{0} to H\textsubscript{2}O\textsubscript{2} in a Haber–Weiss like mechanism during a Fenton reaction is a very slow process at neutral pH (10). The oxidation of Fe\textsuperscript{0} by oxygen results in the formation of an oxide layer, which eventually leads to a reduction in the reactivity of Fe\textsuperscript{0} (6, 11). Several studies have reported different procedures for inhibiting the formation of the oxide layer to maintain or enhance the catalytic activity of Fe\textsuperscript{0}, including the use of sonication (12), external voltage (13), and the introduction of a second metal such as Ag and Pd (14, 15). However, recently, an Fe\textsuperscript{0}/Fe\textsubscript{3}O\textsubscript{4} composite was prepared by mechanical alloying of Fe\textsuperscript{0} and Fe\textsubscript{3}O\textsubscript{4} powders or controlled reduction of FeO\textsubscript{x}H\textsubscript{2x−3} with H\textsubscript{2} and showed highly catalytic activity for the decomposition of H\textsubscript{2}O\textsubscript{2} as a result of an electron-transfer process from metal to magnetite (10, 13).

Based on the redox potentials (eqs 1−3), the composite of iron oxides coated Fe\textsuperscript{0} essentially creates numerous galvanic cells wherein Fe\textsuperscript{3+} serves as the cathode, and iron oxides serve as the anode. The catalytic activity of the composite may be enhanced by electron transfer from Fe\textsuperscript{0} to iron oxides at the metal/oxide interface. In this paper, for the first time, the Fe\textsuperscript{0} surface covered by FeO\textsubscript{x}H\textsubscript{2x−3} was found to be highly effective for the degradation of azodyes at neutral pH and exhibited excellent long-term stability in the presence of H\textsubscript{2}O\textsubscript{2} and UVA. The reaction mechanism was also investigated by determining the generation of *OH radicals under different conditions. Furthermore, the degradation process of ARB was characterized by TOC removal and GC–MS techniques.

Experimental Section

Materials and Reagents. Iron powder (>98.0%) and H\textsubscript{2}O\textsubscript{2} (30%) were chemical reagent grade. Azodyes acid red B (ARB), reactive brilliant red X-3B (X-3B), reactive red K-2G (K-2G), cationic red X-GRL (CRX), and cationic blue X-GRL (CBX) (Figure S1, Supporting Information) were laboratory reagent grade and used without further purification. N,N-diethyl-p-phenylenediamine (DPD) and horseradish peroxidase (POD) were purchased from Sigma-Aldrich. All solutions were prepared with deionized and doubly distilled water, and the solution pH was adjusted by a diluted aqueous solution of NaOH or HCl.

Preparation of Catalysts. Iron powder was calcined at 200 °C for different times (15, 30, 60, and 120 min) in air, and the sample calcined for 30 min (Fe\textsuperscript{0}-30) exhibited the highest activity (Figure S2, Supporting Information). It was interesting to observe that the activity of the catalyst increased rapidly with the cycling times (Figure 1). When the sample was repeatedly used 3 times, the catalyst was filtered, washed with water, and dried at 70 °C for 2 h. Yellow FeO\textsubscript{x}H\textsubscript{2x−3}/Fe\textsuperscript{0} was obtained. The Brunauer–Emmett–Teller (BET) surface area was investigated by the analysis of adsorbed nitrogen. The core X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to monitor the transformation of iron.
area of the sample was 43.6 m²/g and the particle size of FeO₁₋₂ was in the range of 80–100 nm by analysis of SEM (Figure S3, Supporting Information). This catalyst was used for all the experiments unless otherwise specified.

Characterization of Catalysts. The powder X-ray diffraction patterns (XRD) of the catalysts were recorded on a Scintag-XDS-2000 diffractometer with Cu Kα radiation (λ = 1.54059 Å). The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument from Kratos using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV. The infrared spectra were recorded on a Fourier transform infrared (FTIR) spectrophotometer (Nicolet 5700). Samples for FTIR determination were ground with spectrometry-grade chlorotrimethylsilane at room temperature. GC-MS analysis were prepared by the following procedure. The spectrum after 2.5 h reaction time was filtered to remove FeO₁₋₂/Fe²⁺ particles. The solution was evaporated by freeze-dried method. The residue was trimethylsilylated with 0.2 mL of anhydrous pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane at room temperature. GC–MS analysis was carried out on an Agilent 6890GC/5973MSD with a DB-5 MS capillary column.

Results and Discussion

Activity and Stability of Catalyst. As shown in the inset of Figure 1, ln (C₀/C) was highly linear versus time in the first 60 min reaction. The decolorization of ARB followed pseudo-first-order kinetics over FeO₁₋₂-200 in the presence of H₂O₂ with UVA. The reaction rate constant k was 0.0091, 0.0226, and 0.035 min⁻¹, respectively, for the first, second, and third cycle. The activity of FeO₁₋₂ increased rapidly with the cycling times and reached a steady state. Then the catalyst did not exhibit any obvious loss of activity when it was further reused for 10 cycles (Figure 2), indicating that the catalyst had an excellent long-term stability. There was no difference in magnetic strength, and the XPS data did not vary between the samples after repeated use for 3 and 13 times.

Characterization of Catalysts. Figure S4 (Supporting Information) shows the X-ray diffraction patterns of FeO₁₋₂, FeO₁₋₂-200, and FeO₁₋₂-200 after 3 repetitive reactions (FeO₁₋₂-200R). Clearly, calcination at 200 °C did not affect the crystallinity of FeO₁₋₂. FeO₁₋₂ showed similar peaks of XRD patterns with Fe²⁺, which was readily indexed to a cubic phase with FeO²⁻ (JCPDS No.06-0696). The characteristic peaks for Fe²⁺ almost disappeared and new weak diffraction peaks assigned to γ-Fe₂O₃ (20 = 30.33, 35.70, 43.39, 57.46, 63.10; JCPDS No.25-1402) were displayed in FeO₁₋₂-200R, suggesting the formation of an amorphous structure of iron oxide species. To confirm the metallic state of the iron on the surface of the sample, FeO₁₋₂-200R was characterized by XPS analysis. As shown in Figure 3a, the peaks at 711, 719, and 725 eV represented the binding energies of Fe₂p₃/₂, shake-up satellite Fe₂p₃/₂, and Fe₂p₁/₂, respectively. No signal was detected for Fe³⁺ at 707 eV. These features indicated that FeO₁₋₂-200R surface was enclosed with a layer of iron oxide (20, 21). Since both Fe₂O₃ and FeOOH had similar features and peak positions in this region, O1s survey scan was further conducted to delineate the surface oxygen states. As shown in Figure 3b, the O1s region can be decomposed into three peaks at 529.6, 531.0, and 532.2 eV, corresponding to O²⁻, OH⁻, and chemically or physically adsorbed water (20), respectively (O²⁻:OH⁻:H₂O = 57.20:31.93:10.87). The existence of surface OH⁻ group suggested that the oxidized iron was likely in the state of FeOOH. If the surface structure was completely FeOOH, the ratio of O²⁻ to OH⁻ should be approximately 1. However it was less than the experimental value of 1.79, suggesting the existence of Fe₂O₃. To investigate this conjecture, the composition of the surface layer was further confirmed by FTIR measurement. The spectrum of FeO₁₋₂-200R was quite different from that of Fe²⁺ and Fe₂O₃. The peaks at 1635 and 3440 cm⁻¹ were assigned to the O–H bending and stretching of water (22). The bond for Fe–OH bending vibration at 1023 cm⁻¹ was also observed (23). The very weak
90 min of reaction (curve c), while 40% of ARB was degraded exhibited higher activity, 60% of ARB was decolorized after peak at 886 cm$^{-1}$ under otherwise identical conditions. These results indicated that the catalytic mechanism of FeO$_x$H$_{2x}$ was different from that of Fe$^6$. According to a previous work (11), reactive oxygen species could be generated from a reaction between Fe$^6$ and oxygen in the solution, leading to the oxidative degradation of organic compounds, while the oxidation reaction was suppressed in the absence of O$_2$ or by coating iron oxides on the surface of Fe$^6$ (11). Conversely, FeO$_{1-x}$H$_{2x}$ created numerous analogously galvanic cells wherein Fe$^6$ served as the cathode and FeO$_{1-x}$H$_{2x}$ was the anode. Thus the electron transfer from Fe$^6$ to Fe$^{3+}$ was established, resulting in reactive oxygen species. It was possible that O$_2$ hindered the electron-transfer process by trapping electrons, causing the lower reaction activity of FeO$_{1-x}$H$_{2x}$/Fe$^6$ in air than that with N$_2$ atmosphere.

**Detection of Hydroxyl Radicals (·OH).** Since under aerobic condition, the ·OH can be formed by the oxidation of Fe$^6$ (11), in order to further verify the catalytic mechanism of FeO$_{1-x}$H$_{2x}$/Fe$^6$, under deoxygenated conditions in the dark, the generation of ·OH was determined in aqueous Fe$^6$ and FeO$_{1-x}$H$_{2x}$/Fe$^6$ dispersions. As shown in Figure 5, no significant ·OH formation was observed in aqueous Fe$^6$ dispersion (curve a), while the quantities of ·OH increased with the reaction time (curve b) in aqueous FeO$_{1-x}$H$_{2x}$/Fe$^6$ suspension under otherwise identical conditions. According to the published works, in the oxidative electrochemical processes, the initial step is the discharge of water molecules to form adsorbed ·OH at anode surface whether O$_2$ exists or not (26, 27). Therefore, the evidence that ·OH radicals were produced on the surface of FeO$_{1-x}$H$_{2x}$/Fe$^6$ in dark under deoxygenated conditions provides a solid indication that the FeO$_{1-x}$H$_{2x}$/Fe$^6$ possesses the galvanic cell-like performance. With the help of UVA light, the interface electron-transfer process could be enhanced and more quantities of ·OH were produced (curve c), which led to an increase of the catalytic activity of FeO$_{1-x}$H$_{2x}$/Fe$^6$.

**Performance of FeO$_{1-x}$H$_{2x}$/Fe$^6$ in the Presence of H$_2$O$_2$ and UVA.** The catalytic activities of different iron catalysts in the degradation of ARB are shown in Figure 6. With no catalyst, ARB was not significantly degraded in the presence of H$_2$O$_2$ under UV light irradiation at neutral pH (curve a). No significant decolorization of ARB was observed over γ-Fe$_2$O$_3$ (curve d). Some degree of ARB degradation occurred over Fe$^6$ (ca. 50%, curve c) and α-FeOOH (ca. 70%, curve e). However, under otherwise identical conditions, FeO$_{1-x}$H$_{2x}$/Fe$^6$ exhibited the highest catalytic activity toward ARB degradation, and complete decolorization was reached within 60 min (curve f), while the homogeneous reaction (Fe$^{3+}$ concentration in the solution, 1.25 mg/L; the highest concentration detected during the reaction) contributed little to the degradation of ARB (curve b). These results confirmed that the degradation of azodyes came from the synergistic effect of the catalysis of like-galvanic cells and the oxidation of the heterogeneous photo-Fenton reaction in the FeO$_{1-x}$H$_{2x}$/Fe$^6$/H$_2$O$_2$/UVA system according to the reaction mechanism.
the catalyst in the H2O2/UVA system as ARB, and the cationic dyes (CRX and CBX) were degraded efficiently over other azodyes. Both anionic dyes (X-3B and K-2G) and of the degradation of ARB. However, the activity of Fe3+/Fe2+ could not be maintained effectively without the addition of H2O2 in the UVA/catalyst system (Figure S8, Supporting Information). The catalyst was nearly inactive for the degradation of ARB when FeO3H2+/Fe0 was reused for the second time. It was found that the quantities of H2O2 generated from Fe3+/Fe2+ suspension at the second run were much lower than that at the first run (Figure S9, Supporting Information), indicating the interface electron transfer became slow. Higher concentration of Fe3+ in solution in the absence of H2O2 than that in the presence of H2O2 (Figure S10, curves b and d, Supporting Information) also revealed that the electron transfer was hindered from Fe3+ to Fe3+. This result suggested that the addition of hydrogen peroxide played a key role in the catalyst’s long-term stability.

Role of H2O2 and UVA in the Recycling of Fe3+/Fe2+. The changes of iron ion concentration in the solution as a function of irradiation time in air or under deoxygenated conditions at neutral pH are presented in Figure S10 and S11 (Supporting Information). Under air-purged conditions, in the absence of H2O2, the ferrous ion concentration in the solution increased and then decreased to 0.068 mg/L with irradiation time (Figure S10, curve a), while the ferric ion concentration increased and then decreased to 0.645 mg/L (Figure S10, curve b). In the presence of H2O2, the ferrous ion concentration was about 0.1 mg/L in average (Figure S10, curve c), whereas the ferric ion concentration was about 0.41 mg/L (Figure S10, curve d). Figure S11 shows the changes of iron ion concentration when the reaction was conducted under deoxygenated conditions. Without the addition of H2O2, the ferrous ion concentration increased rapidly and reached a maximum concentration of 3.4 mg/L at 40 min, while ferric ions were almost undetectable after 40 min of illumination. The phenomena suggested that the electron transfer from Fe2+ to Fe3+ was inhibited. Conversely, almost no ferrous ions were detected in the presence of hydrogen peroxide (Figure S11, curve c), which indicated that ferrous ions were completely converted to ferric ions. The ferric ion concentration was about 1.57 mg/L. The recycling of ferrous ion to ferric ion is shown in the following equations (eqs 4 and 5). Therefore, the addition of H2O2 increased the recycling of Fe2+/Fe3+ and the oxidation of Fe2+ to Fe3+ resulting in the formation of Fe3+ and FeOOH, leading the decrease of the total iron ion concentration. Besides this, the decrease of iron ion concentration under air-purged conditions may be attributed to the presence of O2.

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Fe^0 + Fe^2+ \rightarrow 2Fe^3+ \quad (4)
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Fe^2+ + H_2O_2 \rightarrow Fe^3+ + \cdot OH + OH^- \quad (5)
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Fe^3+ + 3OH^- \rightarrow Fe(OH)_3 \quad (6)
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Formation of Intermediates. GC–MS was used to monitor the generation of reaction intermediates during the photodegradation of ARB over FeO3H2+/Fe0 in the presence of H2O2 and UVA. The samples treated at 2.5 h of irradiation time were analyzed by GC–MS. All the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 90%. The main products included aromatic acids such as benzoic acid and phthalic acid, and the aliphatic acids propyl acid, malonate, and 2-hydroxy-propanoic acid (Table S1, Supporting Information). About 60% of TOC content was removed when ARB was decolorized completely at 90 min of irradiation (Figure S12, Supporting Information). Subsequently, the TOC of the solution slowly decreased due to the depleted H2O2. The results from GC–MS and TOC analysis suggested that ARB degradation proceeded by the cleavage of the azo bond leading to decolorization and desulfuration, followed by opening of the phenyl and naphthalene rings to form small molecular organic acids. The final step involved was the
further oxidation of the aliphatic acids to produce carbon dioxide and water.

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Supporting Information Available
The results for the structure of the employed azodyes, the catalytic activity of Fe\textsuperscript{0} calcined at 200 °C for different times, SEM, XRD patterns, the generation of H\textsubscript{2}O\textsubscript{2}, the degradation of ARB under different conditions, the concentration of iron ions released from FeO\textsubscript{x}, TOC and GC–MS analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
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