Photoassisted Degradation of Azodyes over $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ in the Presence of H_2O_2 at Neutral pH Values

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Fe^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_2O_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 $\alpha\text{-FeOOH}$ and $\gamma\text{-Fe}_2\text{O}_3$, and the core was Fe^0 ($\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$). $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ 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_2 and small organic acid.

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^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^0 and oxygen. Additionally, Fe^0 has been studied as a precursor of Fe^{2+} in Fenton reactions in acid media (2, 8). The use of Fe^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^- , SO_4^{2-}) is avoided (2); and the remaining Fe^0 can be easily recovered from the solution (2). However, the direct electron transfer from Fe^0 to H_2O_2 in a Haber–Weiss like mechanism during a Fenton reaction is a very slow process at neutral pH (10). The oxidation of Fe^0 by oxygen results in the formation of an oxide layer, which eventually leads to a reduction in the reactivity of Fe^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^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 $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composite was prepared by mechanical alloying of Fe^0 and Fe_3O_4 powders or controlled reduction of Fe_3O_4 with H_2 and showed highly catalytic activity for the decomposition of H_2O_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^0 essentially creates numerous galvanic cells wherein Fe^0 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^0 to iron oxides at the metal/oxide interface. In this paper, for the first time, the Fe^0 surface covered by $\text{FeO}_x\text{H}_{2x-3}$ 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_2O_2 and UVA. The reaction mechanism was also investigated by determining the generation of $\cdot\text{OH}$ 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_2O_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^0 -200) 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 $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ was obtained. The Brunauer–Emmett–Teller (BET) surface

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FIGURE 1. Cyclic degradation of ARB (50 mg/L, 50 mL, pH = 6.95) over the sample that Fe⁰ was calcined at 200 °C in air for 30 min (2 g/L) in the presence of H₂O₂ (13.8 mM) and UVA: (1) first run, (2) second run, (3) third run. The inset shows that the degradation rate of ARB was pseudo-first-order on the irradiation time in the first 60 min reaction.

area of the sample was 43.6 m²/g and the particle size of FeO_xH_{2x-3}/Fe was in the range of 80–100 μm 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 C_{1s} 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 KBr in an agate mortar and IR measurement was carried out at room temperature. Determination of the concentration of H₂O₂ and hydroxyl radicals formed in the catalyst aqueous suspension was performed with a photometric method described in the literature (16–18). Fe²⁺ and Fe³⁺ concentrations were measured by a 1,10-phenanthroline method (19) with a detection limit of 1.8 × 10⁻⁷ mol/L for Fe²⁺.

Procedures and Analysis. The light source was a 300-W high-pressure mercury lamp fixed inside a cylindrical Pyrex flask, which was surrounded by a circulating water jacket to cool the lamp. The exterior of the cylindrical Pyrex flask was wrapped by tinfoil, leaving just a small window (3.5 cm × 1.5 cm) at the side face. The light was then focused onto a 100 mL glass reaction vessel. The average light intensity was 14 mW/cm². To effectively suspend the catalyst, compressed air or N₂ was bubbled from the bottom of the reactor. The reaction temperature was maintained at 25 °C.

Unless noted otherwise, 0.1 g of FeO_xH_{2x-3}/Fe⁰ particles were dispersed in 50 mL azodye solution (50 mg/L, pH = 6.95). Prior to the addition of H₂O₂ (13.8 mM) and UVA irradiation, the suspensions were stirred in the dark for ca. 10 min for the uniform mixture. At given time intervals, 3-mL samples of the aqueous solutions were filtered through a Millipore filter (pore size 0.45 μm) to remove particles. The filtrates were analyzed by recording variations at the wavelength of maximal absorption in the UV–vis spectra of azodyes using a 752N spectrophotometer (Shanghai Precision & Scientific Instruments Co., Ltd., China). The total organic carbon (TOC) of the solution was analyzed with a Phoenix 8000 analyzer. Samples for GC–MS analysis were prepared by the following procedure. The suspension after 2.5 h reaction time was filtered to remove FeO_xH_{2x-3}/Fe⁰ 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

FIGURE 2. Changes in the concentration of ARB (50 mg/L, 50 mL, pH = 6.95) during the multicycle degradation process over Fe⁰.H_{2x-3}/Fe⁰ (2 g/L) in the presence of H₂O₂ (13.8 mM) and UVA.

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 Fe⁰-200 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 Fe⁰-200 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 Fe⁰, Fe⁰-200, and Fe⁰-200 after 3 repetitive reactions (Fe⁰-200R). Clearly, calcination at 200 °C did not affect the crystallinity of Fe⁰. Fe⁰-200 showed similar peaks of XRD patterns with Fe⁰, which was readily indexed to a cubic phase with Fe⁰ (JCPDS No.06-0696). The characteristic peaks for Fe⁰ almost disappeared and new weak diffraction peaks assigned to γ-Fe₂O₃ (2θ = 30.33, 35.70, 43.39, 57.46, 63.10; JCPDS No.25-1402) were displayed in Fe⁰-200R, 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, Fe⁰-200R was characterized by XPS analysis. As shown in Figure 3a, the peaks at 711, 719, and 725 eV represented the binding energies of Fe2p_{3/2}, shake-up satellite Fe2p_{3/2}, and Fe2p_{1/2}, respectively. No signal was detected for Fe⁰ at 707 eV. These features indicated that Fe⁰-200R 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 Fe⁰-200R was quite different from that of Fe⁰ and Fe₂O₃ (Figure 4). 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

FIGURE 3. XPS spectrum of FeO_xH_{2x-3}/Fe⁰: (a) Fe2p, (b) O1s.

FIGURE 4. FTIR spectra of different iron species: (a) Fe⁰, (b) FeO_xH_{2x-3}/Fe⁰, (c) Fe₂O₃.

peak at 886 cm⁻¹ was assigned to α-FeOOH (24), suggesting the existence of FeOOH in the sample. The characteristic peaks at 580 and 450 cm⁻¹ corresponded to the stretching vibration of Fe–O for γ-Fe₂O₃ (25). According to XPS and FTIR analysis, the outer layer of iron oxide was mainly composed of α-FeOOH and γ-Fe₂O₃. Also, hydrogen was generated when Fe⁰-200R was added to the diluted HCl and the particles retained high magnetic strength, indicating the existence of Fe⁰. The catalyst thus had a core–shell structure: the shell was a mixture of α-FeOOH and γ-Fe₂O₃, while the core remained metallic. The catalyst was denoted by FeO_xH_{2x-3}/Fe⁰.

Reaction Mechanism of FeO_xH_{2x-3}/Fe⁰. Degradation of ARB under Different Conditions. As shown in Figure S5 (Supporting Information), ARB was used as a model pollutant to investigate the catalytic activity of different catalysts in the dark both under deoxygenated conditions and in air at neutral pH. In the presence of air, no significant reaction of ARB was observed in the dark over γ-Fe₂O₃ (curve a). Fe⁰ exhibited higher activity, 60% of ARB was decolorized after 90 min of reaction (curve c), while 40% of ARB was degraded over FeO_xH_{2x-3}/Fe⁰ under the same conditions (curve b). In contrast, in deoxygenated solution, ARB was almost completely decolorized after 90 min of reaction over FeO_xH_{2x-3}/Fe⁰ (curve e), while there was nearly no ARB degradation in Fe⁰ suspension under otherwise identical conditions. These results indicated that the catalytic mechanism of FeO_xH_{2x-3}/

FIGURE 5. Hydroxyl radicals generation in Fe⁰ and FeO_xH_{2x-3}/Fe⁰ dispersions (2 g/L) at pH 7.00 as a function of reaction time under deoxygenated conditions: (a) Fe⁰ in the dark, (b) FeO_xH_{2x-3}/Fe⁰ in the dark, (c) FeO_xH_{2x-3}/Fe⁰ under UVA irradiation.

Fe⁰ was different from that of Fe⁰. According to a previous work (11), reactive oxygen species could be generated from a reaction between Fe⁰ and oxygen in the solution, leading to the oxidative degradation of organic compounds, while the oxidation reaction was suppressed in the absence of O₂ or by coating iron oxides on the surface of Fe⁰ (11). Conversely, FeO_xH_{2x-3}/Fe⁰ created numerous analogously galvanic cells wherein Fe⁰ served as the cathode and FeO_xH_{2x-3} was the anode. Thus the electron transfer from Fe⁰ to Fe³⁺ was established, resulting in reactive oxygen species. It was possible that O₂ hindered the electron-transfer process by trapping electrons, causing the lower reaction activity of FeO_xH_{2x-3}/Fe⁰ in air than that with N₂ atmosphere.

Detection of Hydroxyl Radicals (OH[•]). Since under aerobic condition, the OH[•] can be formed by the oxidation of Fe⁰ (11), in order to further verify the catalytic mechanism of FeO_xH_{2x-3}/Fe⁰, under deoxygenated conditions in the dark, the generation of OH[•] was determined in aqueous Fe⁰ and FeO_xH_{2x-3}/Fe⁰ dispersions. As shown in Figure 5, no significant OH[•] formation was observed in aqueous Fe⁰ dispersion (curve a), while the quantities of OH[•] increased with the reaction time (curve b) in aqueous FeO_xH_{2x-3}/Fe⁰ 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 O₂ exists or not (26, 27). Therefore, the evidence that OH[•] radicals were produced on the surface of FeO_xH_{2x-3}/Fe⁰ in dark under deoxygenated conditions provides a solid indication that the FeO_xH_{2x-3}/Fe⁰ 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_xH_{2x-3}/Fe⁰.

Performance of FeO_xH_{2x-3}/Fe⁰ in the Presence of H₂O₂ 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 H₂O₂ under UV light irradiation at neutral pH (curve a). No significant decolorization of ARB was observed over γ-Fe₂O₃ (curve d). Some degree of ARB degradation occurred over Fe⁰ (ca. 50%, curve c) and α-FeOOH (ca. 70%, curve e). However, under otherwise identical conditions, FeO_xH_{2x-3}/Fe⁰ exhibited the highest catalytic activity toward ARB degradation, and complete decolorization was reached within 60 min (curve f), while the homogeneous reaction (Fe³⁺ 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_xH_{2x-3}/Fe⁰/H₂O₂/UVA system according to the reaction mechanism

FIGURE 6. Activity of different iron catalysts (2 g/L) in ARB degradation (50 mg/L, 50 mL, pH = 6.95) in the presence of H_2O_2 (13.8 mM) and UVA: (a) with no catalyst, (b) Fe^{3+} (1.25 mg/L), (c) Fe^0 , (d) $\gamma\text{-Fe}_2\text{O}_3$, (e) $\alpha\text{-FeOOH}$, (f) $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$.

FIGURE 7. Effect of solution pH on the degradation of ARB (50 mg/L, 50 mL) over $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ (2 g/L) in the presence of H_2O_2 (13.8 mM) and UVA: (a) pH = 3.5, (b) pH = 5.0, (c) pH = 7.0, (d) pH = 8.0, (e) pH = 9.0.

of $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$. Furthermore, the photoassisted reaction over $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ can operate efficiently at a wide range of pH in the presence of H_2O_2 (Figure 7). The catalyst exhibited highly catalytic activity for the degradation of ARB from acidic to alkaline (3.5–9.0) and the degradation rate increased with the decrease of initial pH value. However, the outer layer of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ on the surface of Fe^0 may be dissolved when the solution pH = 3.5, leading to the great enhancement of the degradation rate of ARB. The catalyst exhibited high stability when the solution pH changed from 5.0 to 9.0. When the pH was above 5, the balanceable concentration of iron ions released from $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ was 0.62 mg/L at pH = 5, and could not be detected. Subsequently, $\text{Fe}(\text{OH})_3$ formed and partly deposited on the surface of catalyst. However, it did not bring about great influence on the catalyst's activity due to different redox potential on the surface of the catalyst. As shown in Figure S6 (Supporting Information), $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ exhibited highly catalytic activity for the degradation of other azodyes. Both anionic dyes (X-3B and K-2G) and cationic dyes (CRX and CBX) were degraded efficiently over the catalyst in the $\text{H}_2\text{O}_2/\text{UVA}$ system as ARB, and the degradation rates of other dyes were much faster than that of ARB.

Effects of H_2O_2 and UVA on the Activity of $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$. To investigate the influence of H_2O_2 and UVA on the catalytic activity, the decolorization of ARB over $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ at pH 6.95 was performed as shown in Figure S7 (Supporting Information). The single $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ showed lower activity for the degradation of ARB. In contrast, with UVA irradiation or in the presence of H_2O_2 with UVA irradiation, $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ was highly effective for the degradation of ARB. However, the activity of $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ could not be maintained effectively without the addition of H_2O_2 in the UVA/catalyst system (Figure S8, Supporting Information). The catalyst was nearly inactive for the degradation of

ARB when $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ was reused for the second time. It was found that the quantities of H_2O_2 generated from $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ 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 Fe^{3+} in solution in the absence of H_2O_2 than that in the presence of H_2O_2 (Figure S10, curves b and d, Supporting Information) also revealed that the electron transfer was hindered from Fe^{2+} to Fe^{3+} . This result suggested that the addition of hydrogen peroxide played a key role in the catalyst's long-term stability.

Role of H_2O_2 and UVA in the Recycling of $\text{Fe}^{2+}/\text{Fe}^{3+}$. 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 H_2O_2 , 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 H_2O_2 , 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 H_2O_2 , 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 Fe^{2+} to Fe^{3+} 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 H_2O_2 increased the recycling of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the oxidation of Fe^{2+} to Fe^{3+} resulting in the formation of Fe_2O_3 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 O_2 .

Formation of Intermediates. GC–MS was used to monitor the generation of reaction intermediates during the photodegradation of ARB over $\text{FeO}_x\text{H}_{2x-3}/\text{Fe}^0$ in the presence of H_2O_2 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 H_2O_2 . 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 oxidization 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 Fe⁰ calcined at 200 °C for different times, SEM, XRD patterns, the generation of H₂O₂, the degradation of ARB under different conditions, the concentration of iron ions released from FeO_xH_{2x-3}/Fe⁰ during the degradation process, the photodegradation of other azodyes over FeO_xH_{2x-3}/Fe⁰, TOC and GC-MS analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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