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Article

Preparation of a fullerene[60]-iron oxide complex for the photo-fenton degradation of organic contaminants under visible-light irradiation

Cong-yang Zou ^{a,b}, Ze-da Meng ^b, Wen-chao Ji ^a, Shou-qing Liu ^b, Zhemin Shen ^{a,*}, Yuan Zhang ^b, Ni-shan Jiang ^b

^a School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

^b School of Environmental Science and Engineering, Suzhou University of Science and Technology Shihu Campus, Suzhou 215009, Jiangsu, China

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ABSTRACT

Iron oxide (Fe₂O₃) was doped onto fullerene[60] (C₆₀) to form a C₆₀-Fe₂O₃ composite using an easy and scalable impregnation method. The as-prepared C₆₀-Fe₂O₃ samples were characterized by powder X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, high-resolution transmission electron microscopy, UV-vis absorption spectroscopy, Raman spectroscopy, and Fourier transform infrared spectroscopy. The photocatalytic activity of the C₆₀-Fe₂O₃ catalyst was evaluated by examining the degradation of methylene blue (MB), rhodamine B (RhB), methyl orange (MO), and phenol under visible light ($\lambda > 420$ nm) in the presence of hydrogen peroxide. The results showed that the catalyst exhibited excellent catalytic properties over a wide pH range 3.06–10.34. Under optimal conditions, 98.9% discoloration and 71% mineralization of MB were achieved in 80 min. Leaching test results indicated that the leaching of iron from the catalyst was negligible and that the catalyst had a high photocatalytic activity after five reaction cycles. The catalyst was also efficient in the degradation of RhB, MO, and phenol. These findings could be attributed to the synergetic effects of C₆₀ and Fe₂O₃. We used active species trapping experiments to determine the main active oxidant in the photocatalytic reaction process and found that hydroxyl radicals played a major role in the entire process.

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1. Introduction

With rapid industrial development over the past few decades, large volumes of colored dye effluents have created severe environmental pollution problems by releasing toxic and potentially carcinogenic substances into the aqueous phase [1,2]. Waste accumulation has a serious adverse impact on the

environment and is dangerous to human health [3]. Advanced oxidation processes (AOPs) have emerged as promising alternative processes for wastewater treatment, especially for persistent and nonbiodegradable contaminants, such as dyeing wastewater [4–6]. As one of the most important AOPs, photo-Fenton degradation of organic dyes using hydrogen peroxide (H₂O₂)/visible light has been widely studied [7–9]. In this

* Corresponding author. Tel: +86-21-54745262; Fax: +86-21-54742863; E-mail: shenzhemin@sina.com.cn

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process, the photodegradation efficiency depends on the decomposition rate of H_2O_2 . Therefore, developing a photocatalyst to enhance the visible-light-driven activity is important.

Fullerene[60] (C_{60}), which has a unique three-dimensional structure because of its delocalized π electrons, has gained considerable attention; the delocalized conjugated structures of C_{60} molecules allow weak absorption in the visible range and high electron mobility ($>1.3 \text{ cm}^2/\text{V/s}$) [10,11]. Hence, C_{60} can be photochemically activated under visible-light irradiation, resulting in rapid photoinduced charge separation with a high quantum efficiency and relatively slow charge recombination [12–14]. Some recent studies have focused on investigating the utilization of visible light for the treatment of pollutants by coupling C_{60} with other semiconductors with low band gaps [15–18].

Iron oxide (Fe_2O_3) is an abundant, stable, cost-effective, nontoxic, and environmentally benign n-type semiconductor with a band gap of 2.2 eV [19]. Owing to its unique and fascinating physicochemical properties, several researchers have investigated the behavior of Fe_2O_3 in diverse fields such as water splitting [20], catalysis [21], and medicine [22]. Recently, Fe_2O_3 has been used to form hybrid materials with carbon nanomaterials, such as multiwall carbon nanotubes, graphene oxide, and graphene, for the degradation of organic pollutants under visible-light irradiation [23–25]. However, the application of a heterogeneous $\text{C}_{60}\text{-Fe}_2\text{O}_3$ catalyst for the photo-Fenton degradation of organic contaminants has not been reported to date.

In this study, $\text{C}_{60}\text{-Fe}_2\text{O}_3$ composites were prepared for the first time via an easy and scalable impregnation method at 60 °C. The photocatalytic activity of $\text{C}_{60}\text{-Fe}_2\text{O}_3$ was evaluated by examining the degradation of methylene blue (MB), rhodamine B (RhB), and methyl orange (MO) in the presence of H_2O_2 under visible light. The effects of operating parameters, such as initial pH, catalyst dosage, and H_2O_2 dosage, were investigated. A possible mechanism for photo-Fenton degradation was also discussed.

2. Experimental

2.1. Materials

Crystalline fullerene powder (99.9% purity) was purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd. *m*-Chloroperoxybenzoic acid (MCPBA), H_2O_2 (30%, W/W), ferric chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), sulfuric acid (98%), sodium hydroxide, and benzene (99.5%) were purchased from Tianjin Damao Chemical Factory. MB, RhB, and MO were used as model dye pollutants without further purification. All the experiments were conducted using deionized (DI) water.

2.2. Oxidation of fullerene

For the oxidization of C_{60} , MCPBA was used as the oxidizing agent. MCPBA (ca. 1 g) was suspended in 50 mL of benzene, followed by the addition of fullerene (ca. 80 mg). The mixture was heated under reflux in air and stirred for 6 h in a 250 mL

distillation flask. The solvent was then removed at the boiling point of benzene (80 °C). After completion, the dark-brown precipitate was washed with ethyl alcohol and dried at 50 °C to obtain oxidized fullerene.

2.3. Preparation of $\text{C}_{60}\text{-Fe}_2\text{O}_3$

Oxidized C_{60} (ca. 1 g) was added to 100 mL of water and ultrasonically exfoliated in a bath sonicator for 15 min. Then, 20 mL of 0.2 mol/L FeCl_3 solution was added slowly into the aqueous solution of functionalized C_{60} and stirred for 2 h at 60 °C in a 250 mL distillation flask. After the obtained suspension was aged for at least 8 h at 60 °C, the obtained solids were collected and washed five times with DI water. After drying under vacuum at 60 °C for 8 h, a chemically bonded $\text{C}_{60}\text{-Fe}_2\text{O}_3$ composite was finally obtained.

2.4. Characterization

X-ray diffraction (XRD) analysis on a D8 Advance diffractometer (Bruker, Germany) was performed to identify the structure and crystallinity of the as-prepared samples with monochromatic high-intensity $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). High-resolution transmission electron microscopy (HR-TEM) (Tecnai G220, USA) and scanning electron microscopy (SEM, JEOL, Japan) were conducted to analyze the morphology and microstructure of the prepared composites at an acceleration voltage of 200 kV. Fourier transform infrared (FT-IR) spectroscopy (Nicolet 6700; Thermo Ltd., Japan) was carried out to detect the chemical bonds on the surface of the catalyst. The mulls of $\text{C}_{60}\text{-Fe}_2\text{O}_3$ were supported by a KBr plate. UV-vis diffuse reflectance spectra were obtained using a UV-vis spectrophotometer (UV-3600, Shimadzu Ltd., Japan). Photoluminescence measurements were conducted on a fluorescence spectrophotometer (RF-5300PC, Shimadzu, Japan) at room temperature. X-ray photoelectron spectroscopy (XPS; XSAM 800) was employed to characterize the iron states. The binding energies were calibrated with respect to the C 1s peak at 284.6 eV. Peak deconvolution was performed using Gaussian-Lorentzian components after linear background subtraction.

2.5. Photo-Fenton degradation tests and analytical methods

The photocatalytic activity of the $\text{C}_{60}\text{-Fe}_2\text{O}_3$ catalyst was evaluated by examining the degradation of MB, MO, and RhB under visible-light irradiation ($\lambda > 400 \text{ nm}$). A 300 W UV-vis lamp (OSRAM, Germany) was used as a light source. The photo-Fenton degradation of organic compounds was performed in a 100 mL beaker at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$). The reaction beaker was located axially and held in a visible lamp box. The lamp was located at a distance of approximately 100 mm from the aqueous solution in a dark box. The wall of the beaker was shielded from surrounding light with tinfoil. Visible light was obtained with a $\lambda > 400 \text{ nm}$ cut-off filter, which covered the window of the beaker to absorb UV light and allow visible light of $\lambda > 400 \text{ nm}$ to pass through. Around 50 mL of test solution was typically used in the photo-Fenton experiments. The initial

concentration of the dyes was set at 50 mg/L in all experiments. The amount of photocatalytic composite used was 0.02 g/(50 mL solution). A 5 mmol/L H_2O_2 aqueous solution (30%) was added to the reaction solution at the beginning of the irradiation. The reactor was placed on a magnetic churn dasher. The suspension was then irradiated with visible light for a set irradiation time. Visible-light irradiation of the reactor was performed for 20, 40, 60, and 80 min. Samples of approximately 5 mL were withdrawn regularly from the reactor, and dispersed powders were removed using a centrifuge. The clean transparent solution was analyzed using a UV-vis spectrophotometer (UVmini-1240, Shimadzu, Japan). The content of total organic carbon (TOC) was determined with a multi N/C 3100 TOC analyzer (Analytik Jena AG, Germany). In addition, to investigate the iron leaching behavior from the C_{60} - Fe_2O_3 catalyst, the iron ion concentration in solution versus time was determined by atomic absorption spectroscopy (AAS).

3. Results and discussion

3.1. XRD measurements

Using XRD, the phase and structure of C_{60} , oxidized C_{60} , and C_{60} - Fe_2O_3 were investigated. As shown in Fig. 1(a) The characteristic diffraction peaks of oxidized C_{60} appeared at diffraction angles of $2\theta = 10.98^\circ$, 17.9° , and 20.96° ; these diffractions peaks were shifted towards lower angles compared with those of C_{60} and agreed well with the data reported in the literature [26,27]. However, no diffraction peaks corresponding to Fe_2O_3 were detected. This result may be ascribed to the small amount of Fe_2O_3 introduced (Fe content of 3.25 wt%) and the high dispersion of Fe_2O_3 on the surface of C_{60} balls. The diffraction peak of C_{60} - Fe_2O_3 was shifted towards a lower 2θ angle of 17.68° , corresponding to a d -spacing of 5.01 nm. This phenomenon could be attributed to the intercalation of Fe_2O_3 . No impurity peak was found in the C_{60} - Fe_2O_3 hybrid. The average diameter (D) of the as-synthesized C_{60} - Fe_2O_3 particles was calculated as 27.9 nm using the Debye-Scherrer equation [28], $D = Kk/(W\cos\theta)$, at a diffraction angle of 17.68° (2θ). In this equation, W is the breadth of the observed diffraction peak at its half height, K is the so-called shape factor (usually approximately 0.89), and k is the wavelength of the X-ray source used (0.154

Fig. 2. SEM images of C_{60} (a) and C_{60} - Fe_2O_3 (b); TEM image (c) and HR-TEM image (d) of C_{60} - Fe_2O_3 .

nm in our measurements). The calculated D value based on the Debye-Scherrer equation is very similar to that obtained from TEM observations.

3.2. XPS analysis

To further confirm the existence of Fe species and investigate the electronic states of the elements in the catalyst, XPS analysis was performed (Fig. 1(b) and (c)). The XPS spectrum (Fig. 1(b)) shows a composition of C, O, and Fe elements, with three sharp peaks appearing at binding energies of 284.8 (C 1s), 532.4 (O 1s), and 710.9 (Fe 2p) eV. As shown in Fig. 1(c), the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are located at 710.9 and 724.1 eV, respectively; these values are in good agreement with the values of Fe_2O_3 reported in previous literature [29]. Furthermore, a shakeup satellite peak is clearly observed at approximately 719.1 eV, which is characteristic of Fe^{3+} species [30].

3.3. SEM, TEM, and HR-TEM observations

Representative SEM, TEM, and HR-TEM images of oxidized C_{60} and the as-obtained C_{60} - Fe_2O_3 catalyst are given in Fig. 2. In Fig. 2(a) and (b), Fe_2O_3 has a small particle size and good dispersion and the oxidized fullerene clusters are spherical parti-

Fig. 1. (a) XRD patterns of oxidized C_{60} and C_{60} - Fe_2O_3 . The inset shows the XRD pattern of C_{60} ; (b) XPS full survey spectrum of C_{60} - Fe_2O_3 ; (c) XPS Fe 2p spectrum of C_{60} - Fe_2O_3 .

cles with small facets and good dispersion. Comparing Fig. 2(a) and (b), we conjecture that the spherical particles in C_{60} - Fe_2O_3 composites are oxidized fullerene clusters. Fe_2O_3 structures are visible on the C_{60} surface, despite the low doping ratio. TEM was used to obtain additional information about the interfacial region of the fullerene composite.

As shown in Fig. 2(c), fullerene particles can be clearly observed and small clusters of irregularly agglomerated Fe_2O_3 nanoparticles are distributed on the surface of fullerene. Fe_2O_3 nanoparticles with an average particle size of 20–30 nm are dispersed on the spherical fullerene surface. The size data obtained from TEM observations are very similar to the D value calculated from the Debye-Scherrer equation. Further HR-TEM analysis, as shown in Fig. 2(d), revealed a lattice fringe spacing of 0.25 nm, which corresponds to the (110) crystallographic plane of crystalline Fe_2O_3 .

3.4. FT-IR characterization

The chemical structures of oxidized C_{60} and the C_{60} - Fe_2O_3 catalyst, the oxygen-containing functionalities, and their changes after impregnation were confirmed by FT-IR spectroscopy. Fig. 3(a) shows the FT-IR spectra of oxidized C_{60} , Fe_2O_3 , and C_{60} - Fe_2O_3 . The peaks at 591.81, 1097.44, 1403.5, and 1640 cm^{-1} are fundamental infrared active modes consistent with those reported in previous literature; these peaks are attributed to the internal modes of the functionalized C_{60} molecule [31]. The C_{60} - Fe_2O_3 composite also contains these functional groups, and the positions of the peaks are consistent with those of oxidized C_{60} . However, the sharpness of the peaks is different, suggesting some changes in the functional groups of C_{60} - Fe_2O_3 . The peak at 1640 cm^{-1} for oxidized C_{60} shifts to 1630.53 cm^{-1} for C_{60} - Fe_2O_3 and the intensity decreases. A small dip also exists in the spectra at 2377 cm^{-1} because of the presence of atmospheric CO_2 [32]. Moreover, the two distinct absorption bands located at 475.76 and 619.27 cm^{-1} in the photocatalytic samples are attributed to iron–oxygen stretching in γ - Fe_2O_3 . Similar observations have been documented in the literature [33], suggesting that Fe_2O_3 is connected to the –OH groups on the surface of the C_{60} cages [34]. This is in good agreement with the results of the TEM analysis.

3.5. UV-vis diffuse reflectance absorption characterization

Fig. 3(b) shows typical UV-vis diffuse reflectance spectra for C_{60} , Fe_2O_3 , and C_{60} - Fe_2O_3 photocatalysts. The absorption spectrum of pure Fe_2O_3 showed weak absorption in the visible region (400–650 nm). By contrast, the as-prepared C_{60} - Fe_2O_3 nanocomposite showed strong absorption over the visible region (>400 nm). These results suggest that the response of the photocatalyst doped with fullerene to visible light was enhanced; this characteristic has been observed in many fullerene composite materials [35]. In this study, the capability of the C_{60} - Fe_2O_3 material to fully utilize visible light was confirmed by the photodegradation of MB.

3.6. Raman characterization

Raman spectroscopy was used to characterize the crystal structure of the obtained C_{60} - Fe_2O_3 particles. Fig. 3(c) shows the Raman spectra of fullerene and C_{60} - Fe_2O_3 . C_{60} exhibits strong peaks at 1365 and 1588 cm^{-1} . Both spectra indicate the presence of amorphous carbon structures assigned to the pentagonal pinch mode [Ag(2)] and the vibrations of carbon atom domains of C_{60} [36]. Compared with fullerene, the intensity of the Ag(2) peak for the C_{60} - Fe_2O_3 cage was decreased because of the strong π - π stacking interactions between C_{60} molecules and Fe_2O_3 . These findings confirm that Fe_2O_3 is bound to the surface of C_{60} .

3.7. Photo-Fenton degradation of organic dyes

Fig. 4(a) shows the discoloration of MB using the as-prepared catalyst under different conditions. In the reaction system with H_2O_2 and without the C_{60} - Fe_2O_3 catalyst (test a), very little degradation of MB was found after irradiation for 80 min. However, the degradation of MB increased significantly with the C_{60} - Fe_2O_3 catalyst added into the reaction system with (test c) and without H_2O_2 (test b). Therefore, the C_{60} - Fe_2O_3 composite plays a very important role in the decomposition of MB. As shown in Fig. 4(a)d, nearly 70% of MB was degraded by the C_{60} - Fe_2O_3 catalyst after irradiation under visible light for 80 min. This result may be attributed to the efficient separation of

Fig. 3. (a) FT-IR spectra of Fe_2O_3 , oxidized C_{60} , and C_{60} - Fe_2O_3 ; (b) UV-vis diffuse reflectance spectra of C_{60} , Fe_2O_3 , and C_{60} - Fe_2O_3 ; (c) Raman spectra of oxidized C_{60} and C_{60} - Fe_2O_3 .

Fig. 4. (a) Photocatalytic degradation of MB (50 mg/L, 50 mL) using 0.02 g of catalyst under various conditions; (b) Photocatalytic degradation of RhB, MO, or MB (50 mg/L, 50 mL) using 0.02 g C_{60} - Fe_2O_3 and 5 mmol/L H_2O_2 under visible light. The inset shows the TOC removal rate of MB; (c) Degradation of phenol (10 mg/L, 50 mL) under C_{60} - Fe_2O_3 / H_2O_2 /visible light conditions.

photogenerated carriers in the coupled Fe_2O_3 and C_{60} system. As shown in Fig. 4(a)b, approximately 67% of MB was adsorbed in the dark after 80 min. This finding shows that the C_{60} - Fe_2O_3 material has a very high adsorption capacity for MB. The degradation rate of MB was enhanced to 74% (Fig. 4(a)c) when H_2O_2 was added to the reaction solution. However, even in the presence of both H_2O_2 and the catalyst, MB was still not degraded completely in the dark. Meanwhile, nearly 99% of MB was decomposed by the hybrid composite in the presence of H_2O_2 (test e) under visible-light irradiation for 80 min. These results may be ascribed to the remarkable function of the C_{60} - Fe_2O_3 composite, which generates hydroxyl radicals ($\cdot OH$) via the photoelectrochemical decomposition of H_2O_2 under visible light. In order to study the synergetic effects of C_{60} and Fe_2O_3 in the nanocomposite, we used pure Fe_2O_3 and pure C_{60} with H_2O_2 to degrade MB solutions. In the reaction systems with pure Fe_2O_3 or pure C_{60} and H_2O_2 (tests g and h), very little degradation of MB was found after irradiation for 80 min. In contrast, test e revealed that the C_{60} - Fe_2O_3 composite exhibited a good degradation effect. C_{60} - Fe_2O_3 has a much better degradation effect than pure Fe_2O_3 and C_{60} because C_{60} is an energy sensitizer that improves the quantum efficiency and increases the extent of charge transfer. Thus, the synergetic effects of C_{60} and Fe_2O_3 can greatly improve the degradation effect.

To further confirm the catalytic activity of the as-prepared material, the degradation of RhB, MO, and phenol were also examined in the C_{60} - Fe_2O_3 / H_2O_2 /visible light system. As shown

in Fig. 4(b), similar results were observed. Specifically, the discoloration of RhB and MO reached nearly 92% and 86.7% in 120 min, respectively. As shown in Fig. 4(c), the degradation of phenol (50 mL, 10 mg/L) reached 96.1% in 120 min. Therefore, the as-synthesized C_{60} - Fe_2O_3 composite is a high-efficiency photocatalyst in the presence of H_2O_2 under visible light. The results show that carbon-doped photocatalytic materials have a wide range of catalytic properties and can be widely used to degrade organic contaminants, which is consistent with previous reports [37]. The mineralization degree of MB was investigated by measuring the decrease of the TOC. As shown in the inset in Fig. 4(b), the degradation and TOC removal rate of MB in 80 min reached 98.9% and 71%, respectively. Therefore, the C_{60} - Fe_2O_3 / H_2O_2 /visible light system can effectively mineralize MB in solution.

3.8. Effects of parameters on the degradation of MB

3.8.1. Effect of pH

The pH usually has a significant influence on the degradation of organic matter in heterogeneous photo-Fenton reaction processes. When the pH is below 3, $H_3O_2^+$ will form to enhance the stability of H_2O_2 and to scavenge $\cdot OH$. Meanwhile, when the pH is higher than 3, the formation of $\cdot OH$ becomes slow because of the hydrolysis of Fe^{2+} and the precipitation of $FeOOH$ from the system. Fig. 5(a) shows the relationship between the initial pH and the removal efficiency of MB. The discoloration process

Fig. 5. Degradation of MB by the C_{60} - Fe_2O_3 / H_2O_2 /visible light system: (a) effect of pH on the degradation of MB; (b) Effect of C_{60} - Fe_2O_3 dosage on the degradation of MB; (c) Effect of H_2O_2 dosage on the degradation of MB.

remained highly efficient when the pH was 10.34, with a discoloration rate of 96.5%. This result suggests that the C_{60} - Fe_2O_3 catalyst can overcome the drawbacks of a narrow pH range for conventional Fenton reactions. Thus, this catalyst may also be a promising candidate for the degradation of various dyeing wastewaters.

3.8.2. Effect of catalyst dosage

The influence of C_{60} - Fe_2O_3 dosage on the heterogeneous photo-Fenton degradation of MB is shown in Fig. 5(b). The discoloration of MB was significantly influenced by the dosage of the catalyst. The discoloration efficiency of MB increased from 86.4% to 99.3% after irradiation for 80 min when the catalyst dosage increased from 0.2 to 0.4 g/L. The reasons for this increase are twofold: (1) more catalyst could increase the adsorption of MB because additional functionalities are available on the catalyst, and (2) the increased amount of catalyst could increase the number of active sites on the catalyst surface available for the catalytic decomposition of H_2O_2 , generating more $\cdot OH$ [38]. Considering the cost, we chose 0.4 g/L as the optimum catalytic dosage to conduct the following experiments.

3.8.3. Effect of H_2O_2 dosage on MB degradation

The effect of H_2O_2 dosage on the degradation of MB was investigated by varying the initial concentration of H_2O_2 from 1 to 8 mmol/L, as shown in Fig. 5(c). When the dosage of H_2O_2 was increased from 1 to 5 mmol/L, the MB removal velocity improved significantly. The increase in H_2O_2 concentration led to increased formation of $\cdot OH$. However, only a slight increase was observed at higher H_2O_2 concentrations (8 mmol/L). From Fig. 5(c), we conjecture that when the initial concentration of H_2O_2 is high (such as 8 mmol/L), it can act as a scavenger. When the initial concentration of H_2O_2 is low, it can act as radicals (intermediate) for the degradation of organic compounds. This result is observed because H_2O_2 at high concentrations acts as a scavenger of $\cdot OH$ [39].

3.9. Reusability test of C_{60} - Fe_2O_3 composite

To evaluate the reusability of the C_{60} - Fe_2O_3 composite, the catalyst was collected and reused five times to conduct the photocatalytic degradation of MB. As shown in Fig. 6(a), the photodegradation rate of MB still reach over 96% after five cycles. This finding indicates that the catalyst has an excellent photocatalyst stability and a high potential application value.

3.10. Mechanism discussion

To exclude the influence of homogeneous Fenton reactions by iron leached into the aqueous phase, the iron concentration in the reaction solution of MB was monitored during the reaction over 80 min. At the end of the reaction, the amount of leached iron was 0.498 mg/L. This value was negligible compared with the iron content in the C_{60} - Fe_2O_3 catalyst (3.25%). The homogeneous Fenton experiment was performed using iron salts at the same concentration (0.498 mg/L) as that of leached iron. As shown in Fig 4(a)f, the degradation of MB was only 15% after 80 min. Therefore, the homogeneous Fenton reaction made only a very small contribution to MB degradation. Thus, the formation of $\cdot OH$ is probably mainly attributable to the heterogeneous photo-Fenton reaction.

To confirm this assumption, we utilized the fluorescent probe terephthalic acid (TA) to assess $\cdot OH$ formation. The fluorescent probe TA (1.0 mmol/L) was added into the C_{60} - Fe_2O_3 / H_2O_2 /visible light system. TA easily reacted with $\cdot OH$ to form highly fluorescent 2-hydroxyterephthalic acid (HTA). As shown in Fig. 7(a), the fluorescence peak at 426 nm confirmed the formation of $\cdot OH$ during visible irradiation, indicating that $\cdot OH$ was photogenerated in the reaction system. To further confirm that $\cdot OH$ plays a major role in the whole process, we also carried out active species trapping experiments to determine the main active oxidant in the photocatalytic reaction process. Isopropanol (2.0 mL), disodium ethylenediaminetetraacetate (EDTA-2Na) (30 mg), and nitrogen gas were

Fig. 6. (a) Reusability of C_{60} - Fe_2O_3 for the degradation of MB; (b) FT-IR spectra of the as-prepared catalyst and the recycled catalyst after the first run. The inset shows the FT-IR spectrum of pure MB.

Fig. 7. (a) $\cdot\text{OH}$ -trapping photoluminescence spectra for the $\text{C}_{60}\text{-Fe}_2\text{O}_3/\text{H}_2\text{O}_2/\text{visible light}$ system; (b) Active species trapping experiments.

introduced as reactive species scavengers for $\cdot\text{OH}$, holes ($h\nu$), and superoxide anion radicals ($\cdot\text{O}_2^-$), respectively. As shown in Fig. 7(b), the addition of isopropanol greatly reduced the photodegradation rate of MB, whereas the addition of EDTA-2Na and purging with nitrogen gas had relatively weak effects on the photodegradation of MB. Therefore, we can conclude that $\cdot\text{OH}$ is the main oxidant in the reaction system. These findings are consistent with the results for decomposition of MB (Fig. 4(a)e), which shows that $\cdot\text{OH}$ is the main active species.

Based on the above results, we proposed a plausible mechanism for the $\text{C}_{60}\text{-Fe}_2\text{O}_3/\text{H}_2\text{O}_2/\text{visible light}$ catalytic system, as presented in Scheme 1. Firstly, MB is adsorbed on the surface of the $\text{C}_{60}\text{-Fe}_2\text{O}_3$ catalyst. Secondly, as a photosensitizer, when C_{60} is irradiated with visible light, it is excited from the ground state to a short-lived singlet excited state (ca. 1.2 ns), which undergoes rapid intersystem crossing at a rate of $5.0 \times 10^8 \text{ s}^{-1}$ to a lower lying triplet state ($^3\text{C}_{60}^*$) with a long lifetime ($>40 \mu\text{s}$). More importantly, photoexcited fullerenes are also excellent electron acceptors capable of accepting as many as six electrons. $^3\text{C}_{60}^*$ has a higher electron accepting ability than ground state $^1\text{C}_{60}$, and electron-donating compounds can reduce $^3\text{C}_{60}^*$ to give the C_{60} radical anion ($^{\cdot-}\text{C}_{60}$). As the potential

of the conduction band of Fe_2O_3 and the potential of the transformation ($^3\text{C}_{60}^*/^{\cdot-}\text{C}_{60}$) is equal to -0.2 eV , electrons may be transmitted from the conduction band of Fe_2O_3 to $^{\cdot-}\text{C}_{60}$, resulting in the formation of $^{\cdot-}\text{C}_{60}$. This radical species may react further with reactants adsorbed at the interface [40]. C_{60} could use its own photoabsorptive characteristics to absorb electrons from photoinduced irradiation and transfer them to the Fe 3d orbital of Fe_2O_3 to generate Fe^{2+} . Subsequently, the formed Fe^{2+} could react with H_2O_2 to produce $\cdot\text{OH}$. Simultaneously, Fe^{2+} is oxidized into Fe^{3+} to achieve the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle. Next, $\cdot\text{OH}$ degrades MB adsorbed on the surface of the catalyst to CO_2 and H_2O . Finally, the catalyst is restored to the original state. The deposition of C_{60} on the Fe_2O_3 surface is expected to improve the photocatalytic behavior. Fullerene can generate e^-/h^+ pairs under visible-light irradiation. It can be proposed that e^- transfer also occurs in the $\text{C}_{60}\text{-Fe}_2\text{O}_3$ composite between fullerene and Fe_2O_3 , retarding the e^-/h^+ recombination and increasing the photon efficiency [41].

4. Conclusions

In this study, a highly efficient heterogeneous photo-Fenton $\text{C}_{60}\text{-Fe}_2\text{O}_3$ catalyst was successfully prepared by an easy and stable impregnation method. Under the optimum conditions (0.02 g catalyst and 5 mmol/L H_2O_2), 98.9% discoloration and 71% mineralization of MB (50 mg/L) were achieved within 80 min. The $\text{C}_{60}\text{-Fe}_2\text{O}_3$ catalyst showed a high photocatalytic activity over a wide pH range 3.06–10.34. This catalyst was also highly effective for the degradation of MB after five reaction cycles. The results showed that iron leaching from the catalyst was negligible. The catalyst was also effective for the degradation of RhB, MO, and phenol. The $\text{C}_{60}\text{-Fe}_2\text{O}_3$ catalyst has potential as a heterogeneous catalyst for various dyeing wastewater treatments because of its high catalytic activity, wide pH range, good stability, and insignificant iron leaching. We also used active species trapping experiments to reveal the main active oxidant in the photocatalytic reaction process, finding that the hydroxyl radicals play a major role in the entire process.

Scheme 1. Reaction mechanism of the heterogeneous $\text{C}_{60}\text{-Fe}_2\text{O}_3$ photo-Fenton catalyst for the degradation of organics.

Graphical Abstract

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Preparation of a fullerene[60]-iron oxide complex for the photo-fenton degradation of organic contaminants under visible-light irradiation

Cong-yang Zou, Ze-da Meng, Wen-chao Ji, Shou-qing Liu, Zhemin Shen *, Yuan Zhang, Ni-shan Jiang
Shanghai Jiao Tong University; Suzhou University of Science and Technology-Shihu Campus

This is a highly efficient heterogeneous photo-Fenton system. The C₆₀ on the Fe₂O₃ surface is expected to improve the photocatalytic behavior. ·OH plays a major role in the system and degrades the organic compounds to CO₂ and H₂O.

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可见光辐射下富勒烯[60]–氧化铁复合催化剂的制备及光芬顿法降解有机污染物研究

邹丛阳^{a,b}, 孟则达^b, 纪文超^a, 刘守清^b, 申哲民^{a,*}, 张园^b, 蒋妮娜^b

^a上海交通大学环境科学与工程学院, 上海200240

^b苏州科技大学环境科学与工程学院石湖校区, 江苏苏州215009

摘要: 采用简单的可升级的化学浸渍法, 将 Fe_2O_3 掺杂到富勒烯[60](C_{60}) 上, 制得 $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 纳米复合材料. 采用了粉末 X 射线衍射、X 射线光电子能谱 (XPS)、扫描电镜、高分辨透射电镜、紫外-可见吸收光谱、拉曼光谱和傅里叶变换红外光谱, 对其进行了表征. 结果发现, XPS 数据中, $\text{Fe}2p_{3/2}$ 和 $\text{Fe}2p_{1/2}$ 的 XPS 特征峰分别位于结合能 710.9 和 724.1 eV 处, 对应 Fe_2O_3 的 Fe^{3+} . 富勒烯颗粒均匀分散在 Fe_2O_3 纳米颗粒表面, Fe_2O_3 纳米颗粒的平均尺寸大约为 20–30 nm; Fe_2O_3 对于可见光只有微弱的吸收, 而制备出的 $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 纳米复合材料对于可见光有较强的吸收响应.

本文将 $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 纳米复合光催化材料用于光催化降解 50 mL, 20 mg/L MB 和 50 mL, 10 mg/L 苯酚实验. 结果发现, 在双氧水存在下和可见光 (>420 nm) 辐射条件下, $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 对上述有机污染物均有较好的降解效果. 通过测定上述有机物的削减程度, 评估了 $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 催化剂的光催化活性, 通过改变实验条件, 得到可见光/ $\text{C}_{60}\text{-Fe}_2\text{O}_3$ /双氧水体系的最佳光催化降解条件: 在 pH 值为 3.06–10.34 的范围内, 投加 0.02 g 催化剂, 5 mol/L 双氧水. 结果表明, 在最佳条件下, 亚甲基蓝在 80 min 内脱色率能达到 98.9%, 矿化率能达到 71%. 浸出实验的结果表明, $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 复合光催化剂中的铁浸出量可以忽略不计. 经过 5 次循环使用后, $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 复合光催化剂仍具有较高的光催化活性. 为了进一步验证 $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 复合光催化剂的应用广泛性, 本文在可见光/ $\text{C}_{60}\text{-Fe}_2\text{O}_3$ /双氧水体系下, 开展了降解 RhB, MO 和苯酚的试验, 结果发现, 该催化剂它们也具有高的降解效果. 机理研究发现, $\text{C}_{60}\text{-Fe}_2\text{O}_3$ 复合光催化剂的高效催化能力可归因于 C_{60} 和 Fe_2O_3 的协同效应: 在可见光辐射下, 由于 C_{60} 具有独特的光敏性特征, 能够接收电子并把它们转移到 Fe_2O_3 的 $\text{Fe}3d$ 轨道, 并通过一系列反应, 达到 $\text{Fe}^{3+}/\text{Fe}^{2+}$ 循环平衡. 利用活性组分捕集实验, 对光催化反应过程中的主要活性氧化剂进行了区分. 结果表明, 羟基自由基在整个过程中发挥了最主要的作用.

关键词: $\text{C}_{60}\text{-Fe}_2\text{O}_3$; 多相光催化; 光-芬顿; 可见光; 活性成份的捕获

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*通讯联系人. 电话: (021)54745262; 传真: (021)54742863; 电子信箱: shenzhemin@sina.com.cn

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