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# Visible light-induced degradation of organic pollutants using Fe(II) supported on silica gel as an effective catalyst

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**Silica gel-supported Fe(II) (SiOFe) was prepared and used for heterogeneous degradation of sulforhodamine B (SRB) and 2,4-dichlorophenol (DCP) under visible irradiation ($\lambda$ > 420 nm) as an effective catalyst. UV-visible spectra, and infrared Spectrophotometry (IR), fluorescence, total organic carbon (TOC) and electron spin resonance (ESR) measurements were employed to analyze the photoreaction products. The results showed that SRB could be efficiently degraded by SiOFe/$H_2O_2$ system under visible irradiation with 100% decolorization and 72.3% TOC removal after 180 min illumination. The results of ESR and fluorescence measurements indicated that the oxidative process was predominated mainly by the hydroxyl radical (·OH) generated in the system.**

silica gel, sulforhodamine B, heterogeneity, photocatalyst, visible irradiation

Fenton's reagent has been used to treat toxic industrial wastes such as phenols, formaldehyde, benzene derivatives, and complex waste derived from dyestuffs, pesticides, wood preservatives, plastics additives, and rubber chemicals. The process may be applied to treatment of wastewaters, sludge, or contaminated soils to eliminate toxic organic pollutant, improve biodegradability, and reduce biological/chemical oxygen demand and removal of odor and colour. The Fenton reaction has been used for the degradation of organic pollutants in water since it is an efficient and inexpensive way to generate oxidative $^{\cdot}$OH radical[1−3]. However, it still has some disadvantages such as lower effective $H_2O_2$ usage, requiring acidic conditions (pH 3—5) and producing significant amount of ferric hydroxide sludge that requires further separation, which limit its application[4,5]. To overcome these drawbacks, modified Fenton reactions were investigated through modifying the catalysts and/or changing the reaction conditions. For example, introducing light irradiation[6], ultrasonic radiation[7,8] and electrochemical activation[9,10] into the Fenton reaction improved the operation efficiency to some extend.

Loading Fe ion or iron-complexes on solid supports has been found effective to modify the catalysts, and this method is called heterogeneous Fenton catalysts. Various supports have been used in the heterogeneous Fenton reactions. These include resin[11,12], zeolite[13,14], clays[15,16], polyethylene copolymers[17], Nafion film and Nafion/C[4,18], etc. Little work has been reported about using silica gel as the support for the Fenton reaction. Silica gel is a micro-porous material used as support for catalysts due to its unique properties and structure. In the present work, a new heterogeneous Fenton catalyst was prepared by loading $Fe^{2+}$ on silica gel. The catalytic activity of the product was investigated by degradation

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of sulforhodamime B (SRB) and 2,4-dichlorophenol (DCP) under visible light irradiation. UV-vis spectra, IR, fluorescence, TOC and ESR measurements were employed to monitor the process.

## 1 Experimental

### 1.1 Materials

Sulforhodamine B was purchased from Acros (Belgium), and 2,4-dichlorophenol from Beijing Chemical Reagent Company (Beijing, China). Silica gel was obtained from Hailan Co (Qingdao, China) and used as received. 4-Aminoantipyrine was obtained from Wuhan Pharmacy Co (Wuhan, China). All chemicals used were of analytical reagent grade and were used without further purification. NaOH and $HClO_4$ solutions were used to adjust the pH of the solutions. Deionized and doubly distilled water was used throughout this study.

### 1.2 Catalyst preparation

The loading of $Fe^{2+}$ on silica gel was achieved by the method reported by Zheng[19]. The proton of SiOH was then replaced by $Fe^{2+}$ during the loading process.

$$n(-\mathrm{SiO{-}H}) + n/2\mathrm{Fe}^{2+} \rightarrow -(\mathrm{SiO})_n{-}n/2\mathrm{Fe}^{2+} + n\mathrm{H}^+ \quad (1)$$

The amount of $Fe^{2+}$ loaded onto the silica gel support was calculated by measuring the concentration of $Fe^{2+}$ in the residue solution using a standard method[20]. The SiOFe catalysts were separated by filtration, and washed with tap water until no $Fe^{2+}$ could be detected in washing.

The uptake of $Fe^{2+}$ by 1 g silica gel was $3.1\times10^{-4}$ mol when the concentration of $FeSO_4$ used was 4.0 g/L. This product exhibited the highest activity compared with those prepared by using other concentrations of $FeSO_4$. Therefore, it was used throughout all the experiments. The UV-vis diffuse reflectance spectra of SiOFe indicated that the catalyst had an absorption peak at 310 nm and the absorption band extended to 520 nm in the visible region.

### 1.3 Photoreactor and light source

A 500-W halogen lamp (Institute of Electric Light Source, Beijing) was used as the visible light source which was positioned inside a cylindrical pyrex vessel surrounded by a (pyrex) jacket with circulating water to cool the lamp. A cutoff filter (diameter = 3 cm) was used to completely remove the light with wavelength less than 420 nm to ensure that the system was irradiated only by visible light ($\lambda > 420$ nm). The distance between the reaction vessel and light source was 10cm.

### 1.4 Procedures and analyses

All the experiments were carried out in a pyrex vessel (70 mL) in aerated solutions. At given irradiation time intervals, 3mL samples were collected for immediate UV-vis analysis using Hitachi 3010 Spectrophotometer (Hitachi Japan). Also, UV-vis diffuse reflectance spectra of the SiOFe and silica gel blank were determined using the Hitachi 3010 Spectrophotometer equipped with integraph ($\Phi$150 nm). The comparative fluorescence intensity of oxidative radicals was performed on F-4500 Fluorescence Spectrophotometer (Hitachi Japan). The total organic carbon (TOC) values of the degraded solutions were measured by a Multi N/C2100 (Jena Germany) TOC analyzer. DCP concentration was measured by 4-Aminoantipyrine method[21]. Infrared analysis was carried out with a 360FT (Nicolet America) FTIR spectrophotometer. The samples for IR were prepared as follows: the reaction solution was filtered, and the filtrate was evaporated (temperature below 323K) under reduced pressure until water was removed. Then the samples for IR were supported on anhydrous KBr. A Brucker model EPR 300E spectrometer equipped with a Quanta-Ray Nd:YAG laser (355 and 532 nm) was used for the measurement of radicals spin-trapped by DMPO. The settings were center field = 3486.7 G, sweep width = 100.0 G, microwave frequency=9.82 GHz, and power = 5.05 mW.

## 2 Results and discussion

The Fenton reaction can occur in waters under sunlight and the mechanism was understood as:

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe}^{3+} + {}^{\cdot}\mathrm{OH} + \mathrm{OH}^- \quad (2)$$

$$\mathrm{Fe}^{3+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe}^{2+} + {}^{\cdot}\mathrm{OOH} + \mathrm{H}^+ \quad (3)$$

The procedure requires adjusting the wastewater to pH 3—5 before adding slowly a solution of $FeSO_4$ and $H_2O_2$. If the pH is too high, the iron may precipitate as ferric hydroxide, which decomposes the $H_2O_2$ to oxygen catalytically. This reduces the efficiency of the water treatment and can potentially create a hazardous situation. The heterogeneous Fenton catalyst simplifies the reaction by anchoring the iron catalyst onto the silica gel support so that the concentration of iron catalyst is always high on the surface of the solid support (ca. $3.1\times10^{-4}$ mol per gram of silica gel). The porous silica gel structure also enhances the efficiency of hydroxyl radical generation by providing an active surface for the reaction to occur. After the reaction, the catalyst can be easily reused by the sample filtration.

The catalytic properties of this solid-state Fenton catalyst were investigated by the degradation of SRB and DCP (Figure 1).

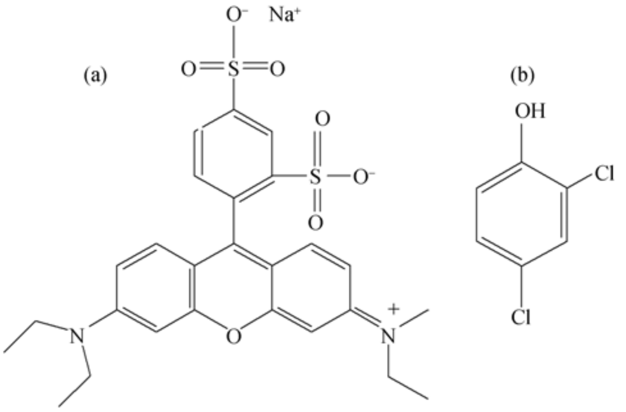

**Figure 1** Chemical structures of SRB (a) and DCP (b).

## 2.1 The generation of ·OH radicals

It was well established that Fenton reactions mainly involved ·OH radical[22]. Spin-trapping ESR was used to study the formation of ˙OH radical (Figure 2). No ESR signals were observed when the reaction was performed in the dark for the aqueous SRB/SiOFe/$H_2O_2$ system in the presence of 5, 5-dimethyl-l-pyrroline-N-oxide (DMPO). Under visible irradiation, the characteristic quartet peaks of DMPO-·OH adduct with an intensity ratio 1∶2∶2∶1 appeared rapidly and the signal stabilized in 80 s irradiation. The results indicated that the solid-state photocatalyst functioned very effectively by rapidly generating ·OH radical derived from hydrogen peroxide.

Benzoic acid reacts with ·OH to generate hydroxyl benzoic acid which has good fluorescence emission at 401 nm when excited at 300 nm[23]. Figure 3 presents the fluorescence intensity at 401 nm after addition of 1ml 0.01 mol/L benzoic acid solution to 2 mL reaction mixtures containing SRB/SiOFe/$H_2O_2$ under visible light illumination. As can be seen from Figure 3, the fluorescence signal of hydroxyl benzoic acid increased gradually and reached maximum intensity in 60 min for the aqueous SRB/SiOFe/$H_2O_2$ system and then dropped down after 80 min irradiation. This observation reflected benzoic acid captured the ·OH that generated in SRB/SiOFe/$H_2O_2$/vis system, and formed hydroxyl benzoic acid. The decline was due to more ·OH needed to oxidize the stable hydroxyl benzoic acid. No fluorescence was observed in the system of vis/SRB/$H_2O_2$/SiOFe/thiourea because ·OH was trapped by thiourea. There was only a small amount of fluorescent product to generate in the systems of SRB/$H_2O_2$/SiOFe/dark and SRB/$H_2O_2$/vis.

## 2.2 The photocatalytic degradation of SRB

The UV-visible spectra changes of SRB in aqueous solution (1.0 mL, $5.0\times10^{-4}$ $mol^{-1}$) with SiOFe dispersions (20 mg) during the degradation process are shown in Figure 4. Under visible light irradiation, the characteristic absorption of SRB at 565 nm decreased rapidly. The complete decomposition of SRB was achieved after 150 min irradiation.

The kinetics plots for the degradation of SRB with and without visible irradiation are illustrated in the inset of Figure 4. In the absence of the catalyst (curve a) or $H_2O_2$ (curve b), the degradation was not observed. No obvious degradation of SRB was found in the dark condition (curve c). However, SRB was rapidly degraded in SRB/SiOFe/$H_2O_2$/vis system (curve d). These results indicated that visible irradiation and the presence of photocatalyst and $H_2O_2$ are necessary for the degradation of SRB.

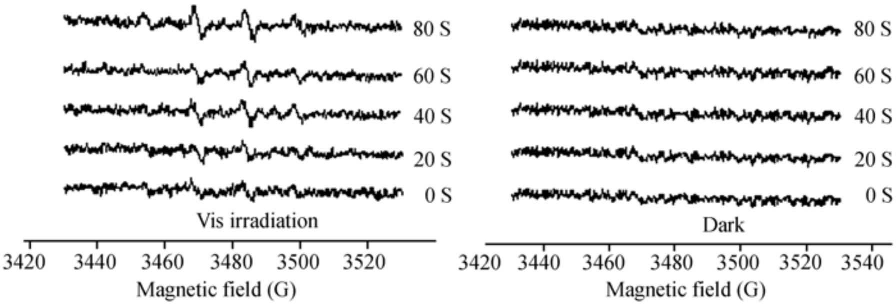

**Figure 2** ESR signals of the DMPO-·OH at pH 3 with 2.0 g·$L^{-1}$ of SiOFe, $0.3\times10^{-2}$ mol·$L^{-1}$ of $H_2O_2$, and $1.5\times10^{-4}$ mol·$L^{-1}$ of SRB.

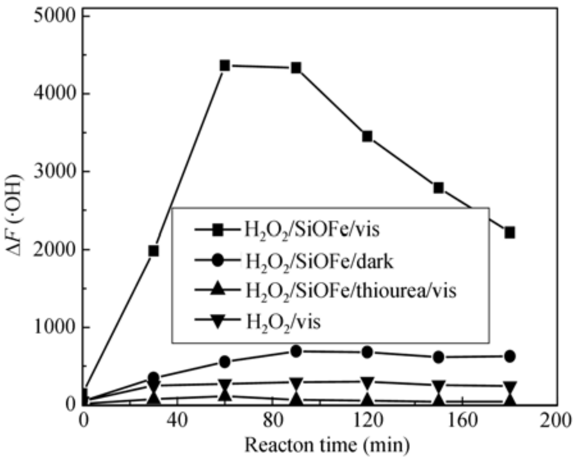

**Figure 3** The fluorescence of 2 mL reaction solution containing 1 mL 0.01 mol/L benzoic acid.

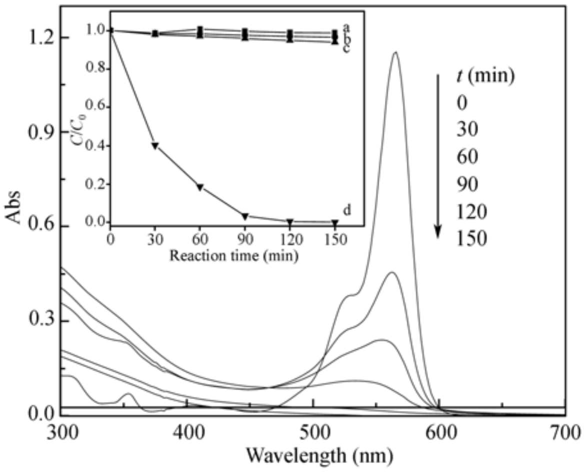

**Figure 4** The temporal UV-vis spectra changes of SRB at pH 3 with 0.4 $g \cdot L^{-1}$ of SiOFe, $7.49\times10^{-4}$ $mol \cdot L^{-1}$ of $H_2O_2$, $1.0\times10^{-5}$ $mol \cdot L^{-1}$ of SRB. Insert: (a) SRB + $H_2O_2$ + visible light; (b) SRB + SiOFe + visible light; (c) SRB + SiOFe + $H_2O_2$ + dark; (d) SRB + SiOFe + $H_2O_2$ + visible light.

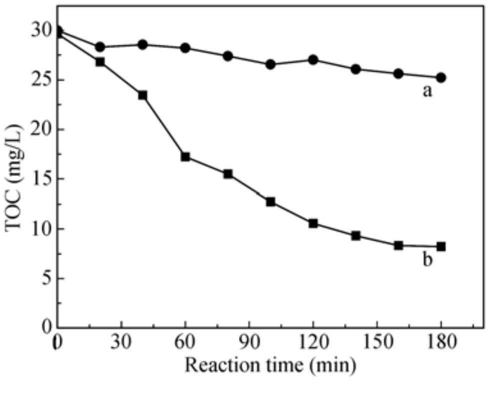

**Figure 5** TOC removal of SRB at pH 3.0 with 0.8 $g \cdot L^{-1}$ of SiOFe, $1.5\times10^{-3}$ $mol \cdot L^{-1}$ of $H_2O_2$, $4.0\times10^{-5}$ $mol \cdot L^{-1}$ of SRB: (a) SRB + SiOFe + $H_2O_2$ + dark; (b) SRB + SiOFe + $H_2O_2$+vis.

### 2.3 The mineralization of SRB

The mineralization degree of the dye was evaluated by the determination of the changes in the total organic carbon (TOC) during the photoreaction (Figure 5). After 180 min, the TOC removal of SRB/SiOFe/$H_2O_2$/vis system was 72.3% (curve b). Without illumination only 10.6% of SRB was mineralized under the same condition (curve a), which confirmed that the visible light and the catalyst could effectively mineralize SRB.

### 2.4 The degradation of 2,4-DCP

DCP was chosen as the substrate since it has no absorption in visible region, the effective degradation of which was mainly attributed to the photocatalytic activity of catalyst. The degradation curve of DCP is displayed in Figure 6, being similar to those obtained for SRB. The degradation could hardly take place for DCP/SiOFe/$H_2O_2$ system in the dark (curve c), or without SiOFe (curve b) or $H_2O_2$ (curve a) under visible irradiation. But the degradation reaction of DCP in the DCP/SiOFe/$H_2O_2$ system was effective under visible irradiation (curve d), in which 80% of DCP was removed after 150 min.

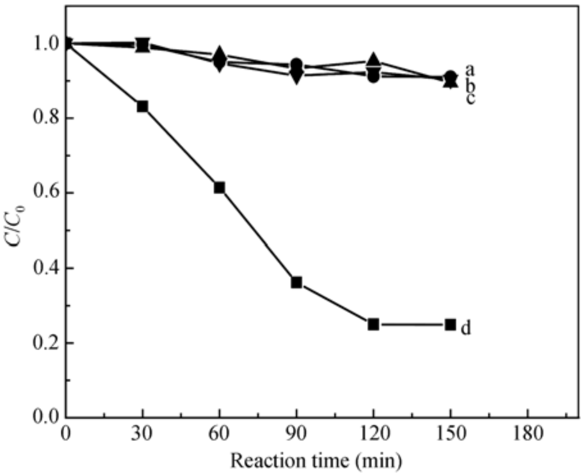

**Figure 6** Photodegradation of 2,4-DCP under different conditions at pH 3 with $3\times10^{-2}$ $mol \cdot L^{-1}$ of DCP: (a) DCP + 1.0 $g \cdot L^{-1}$ SiOFe + visible light, (b) DCP + 0.2 $mol \cdot L^{-1}$ $H_2O_2$ + visible light, (c) DCP + 0.2 $mol \cdot L^{-1}$ $H_2O_2$ + 1.0 $g \cdot L^{-1}$ SiOFe + dark, (d) DCP + 0.2 $mol \cdot L^{-1}$ $H_2O_2$ +1.0 $g \cdot L^{-1}$ SiOFe + visible light.

### 2.5 Catalyst recycling in repetitive degradation of SRB

Repeated degradation experiments were performed to prove the stability and reusability of the proposed photocatalyst in Figure 7. Degradation of 6 consecutive aliquots of $1.0\times10^{-5}$ $mol \cdot L^{-1}$ of SRB at pH 3 with each having $7.49\times10^{-4}$ mol·L$^{-1}$ of $H_2O_2$ and the same amount of SiOFe (20 mg catalyst/50 mL) was carried out. After the first reaction cycle, the catalyst was separated and then reacted with the same amount of SRB and $H_2O_2$. The results of the six cycle experiments are illustrated in Figure 7. The catalyst did not exhibit any significant loss of activity after 3 cycles. It was observed that only 0.8% of Fe$^{2+}$ of the catalyst was detected in the reaction solution after the first cycle (120 min). The accumulative small loss of activity was observed after 5 reaction cycles. These data accounting for the solid catalyst are available for repeated application with little loss of activity.

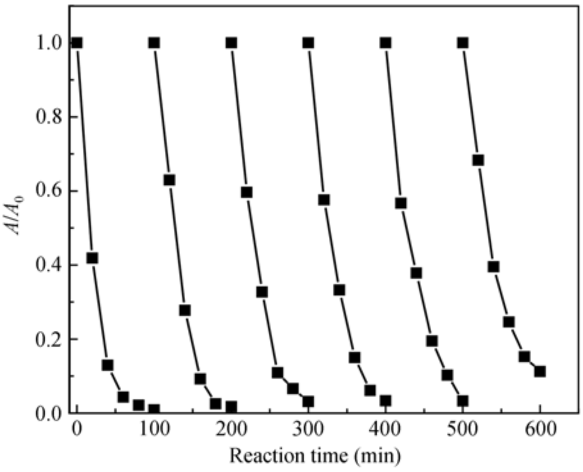

**Figure 7** Catalyst recycling in repetitive degradation of SRB at pH 3 with 0.4 g·L$^{-1}$ of SiOFe, $7.49\times10^{-4}$ mol·L$^{-1}$ of $H_2O_2$, $1.0\times10^{-5}$ mol·L$^{-1}$ of SRB.

## 2.6 IR spectra of the intermediates during degradation

The IR spectroscopy was employed to identify the degradation products of SRB (Figure 8) in the presence of SiOFe and $H_2O_2$ under visible irradiation. The principal bands in the IR spectra of SRB are available in the literatures; the bands at 1590, 1558, 1530, 1510, 1490, and 1470 cm$^{-1}$ corresponded to aromatic ring vibrations, while the band at 1344 cm$^{-1}$ is due to aryl-C bond vibrations[24]. The bands at 1120－1145 cm$^{-1}$ and 628－625 cm$^{-1}$ are caused by vibrations in the $—SO_3^{2-}$ group, the band at 1649 cm$^{-1}$ is attributed to vibrations of the carbon-nitrogen, and the band at 1530－1558 cm$^{-1}$ is due to heterocyclic vibrations. During photo-oxidation, the band of vibrations characteristic of the carbon-nitrogen band (1649 cm$^{-1}$), the aryl-C band (1344 cm$^{-1}$), the aromatic ring, and heterocyclic vibrations (1470－1590 cm$^{-1}$) decreased with decreasing irradiation time and eventually disappeared. The results indicate convincingly that the large conjugated chromophore structure of SRB was destroyed in the presence of SiOFe and $H_2O_2$ under visible irradiation. The absorption bands at 1718, 3300, and 1400 cm$^{-1}$ corresponded to >C=O, —OH of carboxylic acid, and $—CH_3$ or $—CH_2—$ of diethylamine, respectively. These results indicate that the probable mineralized products were amine and carboxylic acid compounds during photo-oxidation. These observations are consistent with the conclusions in other systems in our works[25－27].

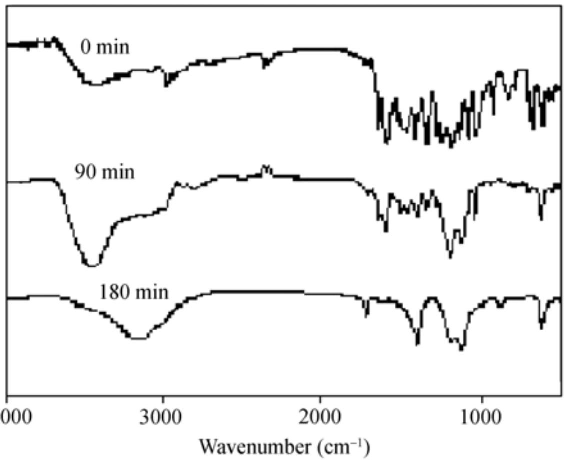

**Figure 8** The IR spectra of the intermediates during degradation of SRB.

## 3 Conclusions

The nonbiodegradable dye sulforhodamine B (SRB) can be efficiently photodegraded in an aqueous solution by using a photocatalytic oxidation system consisting of $H_2O_2$ and Fe$^{2+}$ supported on silica gel. The solid-state catalyst in relation to traditional Fenton regent generates ·OH radicals more rapidly. The decolorization of SRB and TOC removal reached 100% and 72.3% after 180 min, respectively. The photocatalyst can be collected easily from the reaction solution by simple filtration and reused for photocatalytic experiments with little loss of activity.

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