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doi: 10.3866/PKU.WHXB201503023

www.whxb.pku.edu.cn

介孔 Fe/SBA-15 非均相芬顿氧化水中难降解染料罗丹明 B

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摘要: 以介孔二氧化硅 SBA-15 为载体, 采用等体积浸渍法制备了 Fe/SBA-15. 通过 X 射线衍射(XRD)、N₂ 吸附-脱附、扫描电镜(SEM)、透射电镜(TEM)和 X 射线光电子能谱(XPS)等技术对其进行了表征, 并用于对水溶液中罗丹明 B (RhB) 的芬顿氧化. 表征结果表明了 Fe/SBA-15 维持了长程有序的介孔结构, 孔径和比表面积都有所下降, 并呈现棒状体的聚集态, 平均直径为 0.6 μm . Fe 以 $\alpha\text{-Fe}_2\text{O}_3$ 的形态同时存在于介孔孔道内外. 在 Fe/SBA-15 和 H₂O₂ 同时存在条件下 RhB 的去除是吸附和催化氧化降解的协同作用所致, 并且与 Fe/SBA-15 投加量密切相关, 但与初始溶液 pH 几乎无关. 当 Fe/SBA-15 投加量为 0.15 $\text{g} \cdot \text{L}^{-1}$, RhB 初始浓度为 10.0 $\text{mg} \cdot \text{L}^{-1}$, H₂O₂/Fe³⁺ 摩尔比为 2000:1, 初始溶液 pH 为 5.4 和反应温度为 21 $^{\circ}\text{C}$ 时, RhB 去除率达到了 93%. Fe/SBA-15 的 Langmuir 单分子层饱和吸附量为 99.11 $\text{mg} \cdot \text{g}^{-1}$. 此外, 采用 H₂O₂ 浸泡方式对使用过的 Fe/SBA-15 可进行再生, 连续 6 次循环使用后仍可维持 80% 的 RhB 去除率, 且每次使用后 Fe 浸出浓度都在 0.1 $\text{mg} \cdot \text{L}^{-1}$ (或者 0.6% (质量分数)) 以下. 基于淬灭实验、UV-Vis 光谱和气相色谱-质谱(GC-MS)联用仪分析的结果, 提出了 RhB 的去除机理. 非均相芬顿催化剂 Fe/SBA-15 可用于去除像 RhB 这样的生物难降解有机物.

关键词: 非均相芬顿氧化; 吸附; Fe/SBA-15; 罗丹明 B; 羟基自由基

中图分类号: O643

Heterogeneous Fenton Oxidation of Refractory Dye Rhodamine B in Aqueous Solution with Mesoporous Fe/SBA-15

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Abstract: An Fe-loaded mesoporous silica SBA-15, Fe/SBA-15, was prepared by incipient wetness impregnation, characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) techniques and used for heterogeneous Fenton oxidation of dye Rhodamine B (RhB) in aqueous solution. The characterization showed that the Fe/SBA-15 retained a mesoporous structure with a long-range ordered arrangement, reduced pore diameter and surface area, and existed as agglomerates of rod-like crystallites with a mean diameter of 0.6 μm . The Fe species occurred both inside and outside the support pores in the form of $\alpha\text{-Fe}_2\text{O}_3$ crystallites. The removal of RhB in the presence of Fe/SBA-15 and H₂O₂ was shown to be caused by the synergistic effects of adsorption and catalytic oxidative degradation, and was closely related to Fe/SBA-15 dosage. Removal was almost independent of initial solution pH, with approximately 93% achieved at an Fe/SBA-15 dosage of 0.15 $\text{g} \cdot \text{L}^{-1}$, initial RhB concentration of 10.0 $\text{mg} \cdot \text{L}^{-1}$, H₂O₂/Fe³⁺ molar ratio of 2000:1; initial solution pH of 5.4 and 21 $^{\circ}\text{C}$. The Langmuir monolayer adsorption capacity of the Fe/SBA-15 was 99.11 $\text{mg} \cdot \text{g}^{-1}$. In addition, Fe/SBA-15 can be easily regenerated by soaking in H₂O₂ then reused for up to six runs, with RhB removal greater than 80% and Fe leaching below 0.1 $\text{mg} \cdot \text{L}^{-1}$ (or 0.6% (mass fraction)) for each run. A removal mechanism for RhB by Fe/

Received: November 13, 2014; Revised: March 2, 2015; Published on Web: March 2, 2015.

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The project was supported by the Program for Innovative Research Team in Shanghai University, China (IRT 13078).

上海大学创新研究团队计划项目(IRT 13078)资助

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SBA-15 and H_2O_2 was proposed based on the quenching tests, UV-Vis spectra, and gas chromatography-mass spectrometry (GC-MS) analysis. The heterogeneous Fenton catalyst Fe/SBA-15 can be applied to remove non-biodegradable organics such as dye RhB.

Key Words: Heterogeneous Fenton oxidation; Adsorption; Fe/SBA-15; Rhodamine B; Hydroxyl radical

1 Introduction

Textile dyes and other industrial dyestuffs make up one of the largest groups of non-biodegradable materials that impose serious environmental problems because of their existence in the effluents. A number of techniques have been applied to remove refractory organic pollutants from water, such as adsorption,^{1,2} electrochemical oxidation,^{3,4} ultrasonic degradation,^{5,6} photocatalytic degradation,^{7,8} ozonation,^{9,10} etc. Adsorption is easy to operate with high removal efficiency, but it only transfers the pollutants from liquid phase to solid phase, leading to the secondary pollution. The other techniques require special devices and equipment, resulting in the high capital and operational costs. Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has been widely applied in treating organic pollutants in water because it is rapid and inexpensive. However, it has several significant drawbacks such as the acidic pH requirement (pH 2–4), a high Fe dosage generating a large amount of iron sludge, and the limited TOC (total organic carbon) removal.^{11–13} Heterogeneous Fenton oxidation using Fe-based solid materials as catalysts has emerged as a promising alternative to the conventional Fenton process due to the absence of the usual disadvantages and feasibility of the catalyst recycle.

To date, iron-based solid catalysts as promising heterogeneous Fenton catalysts for degradation of organic pollutants have been reported, and can be classified as unsupported iron oxides including Fe_2O_3 , Fe_3O_4 , and zero-valence iron,^{14–16} unsupported iron composites including some non-ferrous metals with variable valence,^{17–19} and supported iron catalysts including iron-immobilized resin,²⁰ membrane,²¹ clay,^{22,23} carbon,^{24–26} zeolite,^{27–29} mesostructured silica materials,^{13,30–45} and alumina.^{46,47}

Mesoporous silica SBA-15, one of the mesoporous molecular sieves, has highly ordered structure, large pore size, and high surface area,^{48,49} which favors the loading and dispersion of the catalytic active components which possess the nano effect due to the nano-size domain. Accordingly, it is possible for Fe loaded mesoporous molecular sieves to exhibit high activity and stability in heterogeneous Fenton oxidation of organic pollutants. Melero *et al.*³¹ investigated a nanocomposite of Fe_2O_3 loaded SBA-15 which acted as an efficient and stable catalyst for wet peroxidation of phenolic aqueous solutions. They also used the SBA-15 loaded Fe_2O_3 and CuO crystallites as the heterogeneous Fenton catalyst, preventing the leaching of Fe species and enhancing the TOC degradation.³² Xiang *et al.*³⁶ synthesized a Fe/SBA-15 by different impregnation and co-condensation approaches, and ascertained the most active catalysts in the total phenol oxidation by H_2O_2 in aqueous solution. Shukla *et al.*³⁷ prepared Fe/SBA-15 by im-

pregnation and tested for adsorption and heterogeneous advanced oxidation of 2,4-dichlorophenol (DCP) in aqueous solution in the presence of H_2O_2 . Botas *et al.*¹³ synthesized various Fe/SBA-15 catalysts for the oxidation of phenol aqueous solution with H_2O_2 . Mayani *et al.*³⁸ evaluated the Fe/SBA-15 for the oxidation of phenols in the presence and absence of H_2O_2 with satisfactory results.

In the previous investigations, phenolic contaminants were usually used as the target substrates, and Fe loaded mesoporous materials were usually regarded as catalysts. Few investigations were concerned with other refractory organic pollutants and the adsorption performance of the catalysts in heterogeneous Fenton oxidation.^{23,27,29,34,37,43} The dye Rhodamine B (RhB) with four *N*-ethyl groups at either side of the xanthene ring and chromophore has the complex molecular structure and stable property, which make it resistant to biological degradation or photodegradation. This paper deals with the dual functions of the prepared Fe/SBA-15 as both an adsorbent and a catalyst in the heterogeneous Fenton oxidation of RhB in aqueous solution. The effects of reaction parameters such as Fe/SBA-15 dosage, initial RhB concentration, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$, and initial solution pH on RhB removal, and the regeneration and recycling performance of the Fe/SBA-15 are examined, and the removal mechanism of RhB from aqueous solution is proposed on the basis of experimental results.

2 Experimental

2.1 Preparation of SBA-15 and Fe/SBA-15

SBA-15 as a support was prepared according to the procedure described by Zhao *et al.*⁴⁸ Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$ (EO: ethoxy; PO: propoxy), Aldrich) and tetra ethyl orthosilicate (TEOS, Aldrich) acted as a template agent and a silica source, respectively. The Fe/SBA-15 with the Fe loading of 10% (mass ratio of Fe to SBA-15, simplified as Fe/SBA-15 in this investigation) was prepared by incipient wetness impregnation. A typical synthesis could be described as follows: the precursor $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, SCRC) was dissolved in deionized water at a concentration dependent on the desired Fe loading, then a certain amount of the prepared SBA-15 was dispersed into the above solution forming a suspension, and the suspension was stirred to make Fe easy to impregnate, and the yielded mixture was dried in oven at 60 °C overnight to evaporate the solvent, finally followed by the calcination at 750 °C for 5 h in air with a heating rate of 10 °C·min⁻¹.

2.2 Characterization of prepared SBA-15 and Fe/SBA-15

The crystalline form of the prepared samples were identified by X-ray diffraction (XRD, Model, Rigaku D/Max-2200X) using a diffraction meter with Cu K_α radiation source of wavelength 0.154056 nm at 40 kV and 40 mA. The small-angle data were collected from 0.5° to 5.0° (2θ) with a scan speed of $0.5^\circ \cdot \text{min}^{-1}$; the wide-angle data were collected from 10° to 80° (2θ) with a scan speed of $5^\circ \cdot \text{min}^{-1}$. N_2 adsorption-desorption isotherms of the samples were acquired using Micromeritics Tristar 3000 apparatus at 77 K. Pore volumes were determined from the data at a relative pressure (p/p_0) of 0.99, the specific surface areas were calculated with BET (Brunner-Emmet-Teller) equation, and pore size distributions were determined by BJH (Barrett-Joyner-Halenda) method according to the adsorption branch of the isotherms. The external morphology of samples was collected on a JSM-6700F scanning electron microscope (SEM). The internal structure of samples was characterized by a JEM-2010F (JEOL) high resolution-transmission electron microscope (HRTEM) with field emission gun at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a ESCALAB 250Xi device.

2.3 Adsorption (adsorption mode)

The adsorption tests were carried out respectively at $\sim 21^\circ\text{C}$ in 100 and 1000 mL glass vessels with 50 and 500 mL of RhB (AR, >99%, SCRC) solutions which were magnetically stirred, respectively. The initial solution pH was not adjusted. Only a known amount of Fe/SBA-15 was added into the aqueous solution to start the contact. The vessel was covered to avoid volatilization. At the end of the contact or at fixed intervals, the suspension samples of 7 mL for each were taken with a syringe. The suspensions were separated by centrifugation at $3500 \text{ r} \cdot \text{min}^{-1}$ for 10 min to obtain the supernatant for analysis.

2.4 Catalytic oxidative degradation (catalytic degradation mode)

The catalytic activity of Fe/SBA-15 was evaluated by the degradation of RhB instead of the adsorption. The catalytic oxidative degradation tests of RhB were carried out respectively at a given temperature in 1000 mL glass vessels with 500 mL of RhB solution for each which was magnetically stirred. The Fe/SBA-15 was first added into the RhB solutions and the suspensions were stirred overnight to achieve the adsorption-desorption equilibrium of RhB. The RhB concentrations at the equilibrium were taken as the initial concentrations (c_0) for the RhB catalytic degradation. Then a given amount of H_2O_2 solution (AR, 30% (w, mass fraction), SCRC) was added into the vessel to initiate the reaction. The vessel was also covered to avoid volatilization. At fixed intervals, the suspension samples of 7 mL for each were taken with a syringe and quenched with excess methanol to stop the reaction. The following procedures were the same as above.

2.5 Combined adsorption and catalytic oxidative degradation (combined mode)

The tests with the combined mode were carried out respectively at $\sim 21^\circ\text{C}$ in 100 and 1000 mL glass vessels with 50 and 500 mL of RhB solutions which were magnetically stirred for 14 h, respectively. The initial solution pH was adjusted by $1.0 \text{ mol} \cdot \text{L}^{-1}$

NaOH and $1.0 \text{ mol} \cdot \text{L}^{-1}$ H_2SO_4 solutions using a pH meter (pHS-3C, Shanghai, China). A known amount of Fe/SBA-15 was added into the aqueous solution, immediately followed by the addition of a given amount of H_2O_2 solution to start the reaction. The subsequent procedures were the same as above.

2.6 Analytical methods

The RhB concentrations were quantified with a UV-Vis spectrophotometer (UV-5300PC, Shanghai) at 552 nm. The Fe concentration in solution was measured by an inductively coupled plasma (ICP) emission spectrometer (Prodigy). The concentration of H_2O_2 in aqueous solution was determined by the titanium complexing method described by Vassilakis *et al.*⁵⁰ The UV-Vis spectra were obtained using a UV-Vis spectrophotometer (UV-5300PC, Shanghai) at different reaction time, with the spectrum scanned from 350 to 650 nm. The principal degradation products of RhB were detected by GC-MS, with an Agilent 7890A gas chromatograph equipped with a DB-5 capillary column (30 mm $\times$ 0.25 mm $\times$ 0.18 mm) combined with an Agilent 5975C mass spectroscopy equipment employed.

Generally, the tests were conducted in duplicate and the errors of the experimental results were below 3%.

3 Results and discussion

3.1 Characterization of SBA-15 and Fe/SBA-15

3.1.1 XRD

The small and wide angle XRD patterns of different samples are shown in Fig.1(a, b), respectively. As seen from the small

Fig.1 Small (a) and wide (b) angle XRD patterns of SBA-15 and Fe/SBA-15

angle XRD patterns (Fig.1(a)), SBA-15 and Fe/SBA-15 exhibit a strong diffraction peak and two obvious sub-peaks, corresponding to the diffraction planes (100), (110), and (200), respectively, indicating that the SBA-15 possesses the typical highly ordered hexagonally mesoporous structure and the Fe/SBA-15 maintains the structure of SBA-15. However, the obvious decrease in intensity of the diffraction peaks in Fe/SBA-15 compared with SBA-15 could be observed, which was attributed to the decrease in average electron density contrast and the formation of iron oxides inside the channels of SBA-15.^{51,52} As seen from Fig.1(b), besides one major peak at 24° for SBA-15 and Fe/SBA-15, there also exist other peaks for Fe/SBA-15 which can be ascribed to the existence of α -Fe₂O₃. Fe₂O₃ is very stable under ambient conditions and is usually the end product of the transformation of other iron oxides.⁵³ Fe₂O₃, Fe₃O₄, and FeO are the principal Fe species available, and the specific species loaded into the supports tend to be dependent on the preparation methods and conditions.^{54–56}

3.1.2 N₂ adsorption-desorption

N₂ adsorption-desorption isotherms and pore size distribution at 77 K of SBA-15 and Fe/SBA-15 are shown in Fig.2. It is evident in Fig.2(a) that Fe/SBA-15 has similar isotherm to SBA-15, exhibiting type IV isotherms with a H1-type hysteresis loop, which was the characteristic of mesoporous materials having cylindrical type mesostructures. For the isotherm of the pure SBA-15, with increased relative pressure, a sharp jump resulting from capillary condensation of N₂ was observed at p/p_0 of 0.6–0.8, while the relative pressure with the emergence of the sharp step

for Fe/SBA-15 decreased to 0.45–0.75, indicating the reduced pore size due to Fe species introduction into the channel of SBA-15. The lower sharp jump of Fe/SBA-15 than that of SBA-15 could also be explained by the reduced order degree of mesoporous structure due to Fe loading. The profiles of pore size distribution (Fig.2(b)) show that the pore sizes of SBA-15 and Fe/SBA-15 are relatively uniform and center at 6–10 nm. The BET specific surface areas and pore parameters of prepared SBA-15 and Fe/SBA-15 are listed in Table 1. The results indicated that loading Fe into SBA-15 reduced the specific surface area, total pore volume, and pore diameter of the support, implying that a fraction of Fe loaded after calcination occupied part of the pore channel of SBA-15.

3.1.3 SEM

The external morphologies of the SBA-15 and Fe/SBA-15 characterized by SEM can be observed from Fig.3. It can be found from Fig.3(a) that the SBA-15 presents the aggregates with the diameter greater than 0.7 μm , consisting of rod-like crystallites with the diameter greater than 0.2 μm and axial length greater than 1.3 μm . It can also be found from Fig.3(b) that the Fe/SBA-15 also displays the aggregates with the diameter more than 0.6 μm , consisting of rod-like crystallites, demonstrating that the Fe loading on SBA-15 does not change the original morphology. There are many small particles attached to the surface of the Fe/SBA-15 (Fig.3(b)), which can be ascribed to the sintering of iron oxides

Fig.2 N₂ adsorption-desorption isotherms (a) and pore size distributions (b) for SBA-15 and Fe/SBA-15

Table 1 Pore parameters of SBA-15 and Fe/SBA-15

Sample	BET specific surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Pore diameter ^a nm
SBA-15	858	1.083	8.260
Fe/SBA-15	460	0.570	7.438

^a calculated from the desorption branch of the isotherm

Fig.3 SEM images of SBA-15 (a) and Fe/SBA-15 (b)

during high-temperature calcination.⁵⁶ The sintering makes a fraction of Fe_2O_3 supported on the surface forming Fe_2O_3 aggregates with the diameter more than $0.4\ \mu\text{m}$.

3.1.4 TEM

The TEM images of the prepared SBA-15 and Fe/SBA-15 are presented in Fig.4. Fig.4(a, b) shows the bright-field images of SBA-15 and Fe/SBA-15, respectively. Fig.(c, d) shows the bright- and dark-field images of Fe/SBA-15, respectively. The highly ordered hexagonal array of SBA-15 with the pore diameter of approximately 7 nm and uniform channel wall thickness of approximately 4 nm is observed from Fig.4(a). Fig.4(b, c, d) displays the representative internal morphology of Fe/SBA-15, the distribution of the supported iron oxides, and a better dispersion of Fe_2O_3 crystallites over the SBA-15 framework. There exist many small black dots (Fig.4(b)) and bright white dots (Fig.4(c, d)) in the images, both dots representing the Fe_2O_3 crystallites

located in the SBA-15 channels. From TEM image inserted in Fig.4(b), the measured lattice spacings of 0.25 nm correspond to (110) interplanar distance of $\alpha\text{-Fe}_2\text{O}_3$. The growth of the crystallites embedded into the SBA-15 channels was limited by the channel walls, thus leading to the rod-like shape of the crystallites. From Fig.4(c), it can be seen that the crystallites have the diameter of approximately 6 nm, consistent with the pore diameter of SBA-15, and the average length more than 25 nm, attributable to the uncontrolled growth of Fe_2O_3 crystallites along the channels. The shaded parts circled in Fig.4(b, c, d) represent a fraction of the aggregates of Fe_2O_3 crystallites loaded outside the channels of SBA-15.

3.1.5 XPS

In the XPS spectra of Fe/SBA-15 composites shown in Fig.5 (a), strong peaks of Fe 2p, Si 2p, and O 1s are observed. In Fig.5 (b), peaks at 711.58 and 724.58 eV are assigned to Fe $2p_{3/2}$ and Fe

Fig.4 TEM images of SBA-15 (a) and Fe/SBA-15 (b, c, d)

Fig.5 XPS analyses of Fe/SBA-15

$2p_{1/2}$ binding energies, which is the main characteristic of Fe^{3+} state.⁵⁷ Additionally, O 1s spectrum of Fe/SBA-15 is shown in Fig.5(c). The main binding energy peak is observed at 532.38 eV, which corresponds to O^{2-} in the iron oxide lattice⁵⁷ and Si 2p binding energy was estimated from Fig.5(d) to be about 103.68 eV.

3.2 Adsorption of RhB on Fe/SBA-15

To understand the adsorption characteristics of mesoporous material Fe/SBA-15, the adsorption tests were carried out in 100 mL glass vessels with 50 mL of RhB solution with an initial RhB concentration from 5.0 to 40.0 $\text{mg} \cdot \text{L}^{-1}$, Fe/SBA-15 dosage of 0.15 $\text{g} \cdot \text{L}^{-1}$, and unadjusted initial pH of 5.4. The contact time and temperature were 14 h and 21 °C, respectively. The adsorption isotherm of RhB on Fe/SBA-15 is presented in Fig.6. As observed, RhB adsorption increases with increasing RhB equilibrium concentration. At the equilibrium concentration of 29.47 $\text{mg} \cdot \text{L}^{-1}$, the RhB adsorption on Fe/SBA-15 is 86.55 $\text{mg} \cdot \text{g}^{-1}$. Two isotherm models, Langmuir (Eq.(1)) and Freundlich (Eq.(2)) isotherms, were applied to fit the experimental data:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where q_e and C_e represent the equilibrium adsorption capacity of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$) and equilibrium concentration of RhB ($\text{mg} \cdot \text{L}^{-1}$), respectively, $q_{\max}$ is monolayer adsorption capacity of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$), K_L is the Langmuir adsorption constant ($\text{L} \cdot \text{mg}^{-1}$), K_F ($\text{L} \cdot \text{mg}^{-1}$) and n (dimensionless) are the Freundlich constants, related to the adsorption capacity and adsorption intensity, respectively. The parameters of the fitted curves of two isotherms are listed in Table 2. As seen, the fitted curve of Langmuir isotherm ($R^2=0.9976$) is more reasonable than that of

Fig.6 Adsorption curve of RhB on Fe/SBA-15

Fe/SBA-15 dosage: 0.15 $\text{g} \cdot \text{L}^{-1}$, unadjusted initial solution pH (5.4), T: 21 °C

Table 2 Parameters of Langmuir and Freundlich isotherms

Adsorbent	Langmuir			Freundlich		
	$q_{\max}/(\text{mg} \cdot \text{L}^{-1})$	$K_L/(\text{L} \cdot \text{mg}^{-1})$	R^2	$K_F/(\text{L} \cdot \text{mg}^{-1})$	n	R^2
Fe/SBA-15	99.11	0.21	0.9976	23.16	2.37	0.9217

Freundlich one ($R^2=0.9217$). $q_{\max}$ of 99.11 $\text{mg} \cdot \text{g}^{-1}$ from Langmuir isotherm represents a complete monolayer adsorption capacity of RhB on the Fe/SBA-15 surface.

The substantial characteristic of Langmuir isotherm can be shown as the equilibrium parameter R_L (dimensionless), which is defined as follows:¹

$$R_L = \frac{1}{1 + C_0 K_L} \quad (3)$$

where C_0 is the initial adsorbate concentration ($\text{mg} \cdot \text{L}^{-1}$), R_L is a characteristic value for the adsorption process. It is generally accepted that $R_L > 1$ represents an unfavorable adsorption process, with $0 < R_L < 1$ favorable, $R_L = 1$ linear, and $R_L = 0$ irreversible adsorption process. Given $K_L = 0.21 \text{ L} \cdot \text{mg}^{-1}$, and initial RhB concentrations at 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, and 40.0 $\text{mg} \cdot \text{L}^{-1}$ respectively, all the R_L values calculated in this investigation ranged between 0 and 1, indicating that the RhB adsorption on SBA-15 is a favorable process and the Fe/SBA-15 may be used as an efficient adsorbent.

As shown in Table 3,⁵⁸⁻⁶² the Fe/SBA-15 possesses higher adsorption capacity than fly ash, MIF-B, Fe-Ben, and BiFeO_3 , etc, but lower capacity than SBA-15. The maximum adsorption capacity of pure SBA-15 for Rhodamine B was determined to be 497.9 $\text{mg} \cdot \text{g}^{-1}$.⁶² When Fe was supported on SBA-15, the adsorption capacity of Fe/SBA-15 was reduced since $\alpha\text{-Fe}_2\text{O}_3$ was introduced into the SBA-15 channel. The high adsorption capacity provides adequate adsorption sites, and also benefits the subsequent heterogeneous catalytic reaction.

3.3 Effect of various reaction parameters on RhB removal with combined mode

3.3.1 Preliminary test

As a preliminary test, the variation of RhB concentrations in aqueous solution with time under three different operation modes was investigated: adsorption, catalytic degradation, combined adsorption and catalytic degradation, and the results are shown in Fig.7. The corresponding operation conditions are Fe/SBA-15 dosage at 0.15 $\text{g} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ at 2000:1, initial RhB concentration at 10.0 $\text{mg} \cdot \text{L}^{-1}$, initial solution pH at 5.4 (unadjusted), and reaction temperature at 21 °C.

As seen from Fig.7, in the absence of H_2O_2 , the Fe/SBA-15 exhibits the RhB adsorption removal up to 55%, and the ad-

Table 3 Comparison of RhB adsorption on different adsorbents (Langmuir isotherms)

Adsorbent	Maximum adsorption capacity/($\text{mg} \cdot \text{g}^{-1}$)	Reference
molecular imprinted fiber (MIF-B)	19.0 (pH=7)	58
fly ash	10.0 (pH=12)	59
iron-pillared bentonite (Fe-Ben)	98.6 (pH=5)	60
BiFeO_3	11.9 (pH=4.0); 2.5 (pH=6.86)	61
SBA-15	497.9 (unadjusted solution pH=5.4)	62
Fe/SBA-15	99.1 (unadjusted solution pH=5.4)	this work

Fig.7 Removal of RhB in aqueous solution under three operational modes

Fe/SBA-15 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, C_{RhB} : $10.0 \text{ mg} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 2000:1, no pH adjustment (5.4), T : 21°C

sorption is very fast within the initial 60 min resulting in approximately 50% RhB removal and attains a plateau in 120 min (curve a). The Fe/SBA-15 is an efficient catalyst for Fenton oxidation, and the catalytic oxidative degradation of RhB is able to take place at a significant but quite uniform rate, with 84% RhB removal achieved (curve c). In the presence of both Fe/SBA-15 and H_2O_2 in the RhB solution, the change of RhB concentrations with time is different from the above-mentioned two variations, attaining the RhB removal of 93%, and is also not equal to the simple sum of the adsorption and catalytic degradation contributions (curve b), which demonstrates the existence of the synergic effect of adsorption and catalytic degradation for RhB removal.

3.3.2 Effect of Fe/SBA-15 dosage

The effect of Fe/SBA-15 dosage on RhB removal in the presence of H_2O_2 is presented in Fig.8. As observed, in the presence of H_2O_2 without Fe/SBA-15, the RhB removal is only 17%, illustrating that H_2O_2 alone fails to oxidize RhB effectively. The increase in Fe/SBA-15 dosage from 0 to $0.15 \text{ g} \cdot \text{L}^{-1}$ leads to a significant increase of RhB removal to 94%, but the further increase in Fe/SBA-15 dosage from 0.15 to $0.30 \text{ g} \cdot \text{L}^{-1}$ results in only a slight increase of RhB removal, approaching the upper removal limit. The increased Fe/SBA-15 dosage would increase

Fig.8 Effect of Fe/SBA-15 dosage on RhB removal

C_{RhB} : $5.0 \text{ mg} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 1500:1, pH: 3.0, T : 21°C

adsorption sites for reactants and also provide more catalytic active sites for activation of H_2O_2 to generate more hydroxyl radicals, thus leading to a remarkable enhancement of the RhB removal efficiency and removal rate.

3.3.3 Effect of initial RhB concentration

Fig.9 displays the RhB removal at various initial RhB concentrations. As shown, the lower initial RhB concentrations in aqueous solution with the fixed dosages of Fe/SBA-15 and H_2O_2 favor the RhB removal. The RhB removal in 14 h declines from 92% to 37% as the initial RhB concentration increases from 5.0 to $50.0 \text{ mg} \cdot \text{L}^{-1}$. This can be ascribed to the following reasons: (1) The fixed dosage of Fe/SBA-15 and H_2O_2 generates the fixed $\text{HO}^\bullet$ amount, and with higher RhB initial concentration, the amount of RhB molecules per unit volume is larger, causing the decrease in the percentage of RhB molecule involved into the reaction and the decrease of the removal. (2) The active sites blockage arising from more carbonaceous deposit on the Fe/SBA-15 for higher RhB concentration may lead to the decline in catalytic activity of Fe/SBA-15. A few investigations have presented the similar conclusion that the higher the dye concentration, the more the removal of the dye is suppressed.^{15,22}

3.3.4 Effect of initial solution pH

The effect of initial solution pH on RhB removal in the presence of Fe/SBA-15 and H_2O_2 was investigated to demonstrate the different pH effect between the present heterogeneous Fenton oxidation and conventional homogeneous Fenton reaction. Fig.10 displays the RhB removal at various initial pH ranging from 3 to 9 including the unadjusted initial solution pH of 5.4. As observed, the RhB removal efficiency and rate changes little with initial solution pH. The RhB removal ranged approximately from 82% to 93% at the pH from 3.0 to 9.0, with the maximum removal of 93% at pH 5.4. Accordingly, this heterogeneous Fenton oxidation has the significant advantages over conventional homogeneous Fenton oxidation processes, removing the pH adjustment requirement and promoting the practical applications. The removal of RhB under the combined adsorption and catalytic degradation mode is closely related to the surface properties of Fe/SBA-15 and the distribution of the RhB species, etc. in aqueous solution, all of

Fig.9 Effect of initial RhB concentration in aqueous solution on RhB removal

Fe/SBA-15 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 1500:1, pH: 3.0, T : 21°C

Fig.10 Effect of initial solution pH on RhB removal

Fe/SBA-15 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, C_{RhB} : $10.0 \text{ mg} \cdot \text{L}^{-1}$,
molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 1500:1, T : 21°C

which are dependent on the solution pH. The combined dependence of the several factors on the pH results in the above effect of initial solution pH.

3.3.5 Effect of molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$

Fig.11 presents the effect of initial H_2O_2 concentrations (in terms of molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$) on RhB removal in the presence of Fe/SBA-15. As observed, RhB removal reaches 55% in the presence of Fe/SBA-15 without any oxidant H_2O_2 , which can be attributed to the RhB adsorption on Fe/SBA-15. The higher the molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ in the range of 0:1 to 2000:1 at the Fe/SBA-15 dosage of $0.15 \text{ g} \cdot \text{L}^{-1}$, initial RhB concentration of $10.0 \text{ mg} \cdot \text{L}^{-1}$, initial solution pH of 3.0, and 21°C , the higher the removal efficiency and rate of the RhB. However, the further improvement of RhB removal was not significant at the $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ molar ratio ranging from 2000:1 to 2500:1. It is known that for the heterogeneous Fenton reaction more hydroxyl radicals, hence higher RhB removal, are available at higher initial H_2O_2 concentrations. Nevertheless, H_2O_2 can also act as a hydroxyl radical scavenger as described in Eqs.(4) and (5), and can also take place the self-decomposition as described in Eq.(6), so the further increase of the H_2O_2 concentration cannot result in the significant increase of hydroxyl radicals and the enhancement of the RhB removal.

Fig.11 Effect of molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ on RhB removal

Fe/SBA-15 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, C_{RhB} : $10.0 \text{ mg} \cdot \text{L}^{-1}$, pH: 3.0, T : 21°C

3.4 Reusability of the Fe/SBA-15

In the case of removing organic pollutants in heterogeneous Fenton oxidation system, the reusability of Fenton catalyst tends to be one of the technical advantages. The reusability of catalyst is reflected by the catalytic activity and stability of the catalyst. The catalytic activity of the Fe/SBA-15 can be evaluated by the removal of RhB in aqueous solution in the presence of H_2O_2 and used Fe/SBA-15, while the stability of the Fe/SBA-15 can be estimated by the leaching of Fe. The results are presented in Figs.12 and 13. The H_2O_2 soaking technique was employed to treat the used Fe/SBA-15 for the next run as follows: the used solid Fe/SBA-15 was collected by suction filtration with $0.22 \mu\text{m}$ membrane, then soaked in $5 \text{ mol} \cdot \text{L}^{-1}$ H_2O_2 solution for one night, and finally dried in oven at 80°C for 5 h. The H_2O_2 soaking technique is not only simple in operation, but also inexpensive, and is better than the calcination technique employed by other researchers.^{32,33} The performance difference between the untreated Fe/SBA-15 and the treated one is displayed in the inset of Fig.12, showing a

Fig.12 Variation of removal of RhB with time during six recycled runs of Fe/SBA-15

Fe/SBA-1 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, C_{RhB} : $10.0 \text{ mg} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 2000:1, pH: 5.4 (unadjusted), T : 21°C

Fig.13 Fe leaching during six recycled runs of Fe/SBA-15

significant drop in the performance, adsorptive and catalytic, for the used Fe/SBA-15 without any treatment. In the reuse tests of the Fe/SBA-15, several parallel tests were carried out in every run until the last one to ensure that the Fe/SBA-15 amount was sufficient for the next run. As shown in Fig.12, the performance of the used Fe/SBA-15 suffers slight decline in RhB removal during 6 recycled runs, with RhB removal of approximately 90% for the 1st run and approximately 80% for the 6th run.

Additionally, the Fe leaching from the heterogeneous catalyst may be also responsible for the decrease in the number of active sites, hence the catalytic activity²². The Fe leaching was investigated and the results are presented in Fig.13. For any one of the six runs, the Fe leaching concentration and leaching percent are less than $0.1 \text{ mg} \cdot \text{L}^{-1}$ and 0.6%, respectively (Fig.13). Such a low Fe leaching does not pose the contaminated water. The total Fe leaching percent after the six runs was calculated to be approximately 3.2%, which is a lower Fe leaching and sustains the stable catalytic activity of Fe/SBA-15. It was reported that some heterogeneous Fe catalysts were reused in the successive Fenton-like oxidation runs with significant Fe lost and most poorly-bounded iron species lost during the first run³².

3.5 RhB removal mechanism in the presence of Fe/SBA-15 and H_2O_2

3.5.1 Comparison of homogeneous and heterogeneous Fenton reaction for RhB removal

Fig.14 presents the comparison of RhB removal in the presence of H_2O_2 and heterogeneous Fe/SBA-15 or homogeneous Fe(III). As observed, RhB removal (degradation) in the homogeneous Fe(III)- H_2O_2 system shows similar behavior, with the degradation efficiency increasing with increasing Fe^{3+} concentration and degradation rate keeping relatively slow in the process. The degradation of RhB in 14 h enhanced from 18% to 28% as Fe^{3+} concentration increased from 0.1 to $1.0 \text{ mg} \cdot \text{L}^{-1}$, indicating that $1.0 \text{ mg} \cdot \text{L}^{-1}$ of Fe^{3+} concentration was not high enough to attain the significant decomposition of RhB. RhB removal in the heterogeneous Fe/SBA-15- H_2O_2 -RhB system was much faster than that in the homogeneous Fe(III)- H_2O_2 system with up to $1.0 \text{ mg} \cdot \text{L}^{-1}$ of

Fe^{3+} concentration. For the heterogeneous system, almost complete RhB removal could be achieved in 14 h with Fe leaching less than $0.1 \text{ mg} \cdot \text{L}^{-1}$. Based on the comparison, it is believed that the heterogeneous Fe/SBA-15 instead of the Fe^{3+} leached in the solution is responsible for the RhB removal, i.e., the homogeneous reaction initiated by the leached Fe^{3+} has little effect on the RhB removal.

3.5.2 Quenching tests

In order to confirm whether the RhB degradation in the presence of Fe/SBA-15 and H_2O_2 involves the hydroxyl radicals ($\text{HO}^\bullet$), free radicals quenching tests were conducted with *tert*-butanol, an efficient hydroxyl radical scavenger with the reaction rate of $3.8 \times 10^8 - 7.6 \times 10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$,⁶¹ and the result is shown in Fig.15. As observed, the removal efficiency of RhB in the absence of *tert*-butanol in the Fe/SBA-15- H_2O_2 -RhB system is 93%, but the presence of *tert*-butanol in the system remarkably suppresses the RhB removal efficiency and rate, indicating that a large number of hydroxyl radicals ($\text{HO}^\bullet$) are scavenged by *tert*-butanol. Therefore, the primary approach of the RhB degradation with the couple of Fe/SBA-15 and H_2O_2 is for hydroxyl radicals from the H_2O_2 to attack the targeted RhB. In conclusion, the primary identified reactive radical in the heterogeneous Fenton system is hydroxyl radical, $\text{HO}^\bullet$.

3.5.3 UV-Vis spectra of RhB degradation

Fig.16 shows the temporal absorption spectrum changes of RhB degradation in the presence of Fe/SBA-15 and H_2O_2 . It is generally accepted that there exist two competitive processes for RhB degradation: one is N-de-ethylation, and the other is the destruction of the conjugated structure.^{63,64} Based on Fig.15, the following explanations can be made. First, the phenomenon that characteristic absorption peak at 552 nm rapidly decreased and almost disappeared over time manifested the destruction of conjugated xanthene structure, and meanwhile no new band occurrence obviously eliminated the possibility of any complex formation originated from Fe/SBA-15, H_2O_2 , and RhB. This is coincident with the results reported in other literature.^{4,15,65} Second, the maximum absorption band of the solution appeared blue shift resulted from the formation of series of N-de-ethylated interme-

Fig.14 Comparison of homogeneous and heterogeneous Fenton reactions for RhB removal

(a) Fe^{3+} : $0.1 \text{ mg} \cdot \text{L}^{-1}$, (b) Fe^{3+} : $0.5 \text{ mg} \cdot \text{L}^{-1}$, (c) Fe^{3+} : $1.0 \text{ mg} \cdot \text{L}^{-1}$, (d) Fe/SBA-1: $0.15 \text{ g} \cdot \text{L}^{-1}$; C_{RhB} : $10.0 \text{ mg} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 2000:1, pH: 5.4, T : 21°C

Fig.15 Effect of hydroxyl radical scavenger on removal of RhB

Fe/SBA-15 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, C_{RhB} : $10.0 \text{ mg} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 2000:1, pH: 5.4 (unadjusted), T : 21°C

Fig.16 UV-Vis absorption spectra of RhB removal in the presence of Fe/SBA-15 and H_2O_2

Fe/SBA-15 dosage: $0.15 \text{ g} \cdot \text{L}^{-1}$, $C_{\text{RhB}}: 10.0 \text{ mg} \cdot \text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$: 2000:1, pH: 5.4 (unadjusted), T : 21 $^\circ\text{C}$

diates, indicating that the energy required for electron transition may be elevated and RhB molecular structure has changed in degradation process. Nevertheless, the blue shift of the absorption band observed was insignificant, with its shift numbers as $\Delta\lambda=13 \text{ nm}$ (553–540 nm). Consequently, it can be deduced from the spectral changes that the ring-opening happened simultaneously with N-de-ethylation during the degradation process, and compared with N-de-ethylation process, the destruction of conjugated xanthene structure played a dominant role in our system.

3.5.4 GC-MS analysis of RhB degradation products

The GC-MS analysis of the supernatant phase is very useful for acquiring the information about the degradation products. Before GC-MS analysis, sample derivatization of the resultant solution coupled with the extraction with organic solvent methylene chloride was carried out. The GC-MS analysis results for the samples generated from the Fe/SBA-15- H_2O_2 -RhB system are presented in Table 4. The degradation products can be divided into two groups: the aromatic compounds with different substituent groups, and the organics with relatively lower molecular weights, most of which are organic acid and alcohol. Among the degradation products, the content of glycerol is the highest, which is evidence that RhB suffered the destruction of the conjugated structure and decomposed into simple organics which can be easily converted to CO_2 and H_2O .

3.5.5 Pathway of removing RhB from aqueous solution

In this investigation, XRD characterization showed that the Fe species occurred in the support in the form of $\alpha\text{-Fe}_2\text{O}_3$ crystallites, and other experimental results demonstrated that heterogeneous Fe/SBA-15 instead of the Fe^{3+} leached in the solution was responsible for the Fenton oxidation of RhB. It has been reported that heterogeneous Fenton oxidation occurs mainly on the surface of solid catalyst *via* Fe oxide active sites, which promote the formation of peroxide radicals.³⁷ Under acidic and neutral pH conditions for our heterogeneous system, the radical reaction pathway, which is initiated by the formation of a complex between the $\text{SiO}_2\text{-Fe}^{\text{III}}$ and H_2O_2 on the interface, may be proposed as follows:

Table 4 Principal by-products of RhB removal detected by GC-MS

No.	Retention time/min	Identified by-product	Structure formula
1	4.93	acetic acid	<chem>CC(=O)O</chem>
2	5.91	malonic acid	<chem>OC(=O)CC(=O)O</chem>
3	6.41	glycerol	<chem>OCC(O)CO</chem>
4	6.78	glyceric acid	<chem>OC(=O)C(O)CO</chem>
5	7.85	malic acid	<chem>OC(=O)C(O)CC(=O)O</chem>
6	8.03	adipic acid	<chem>OC(=O)CCCCC(=O)O</chem>
7	9.21	phthalic acid	<chem>O=C(O)c1ccccc1C(=O)O</chem>
8	9.61	isophthalic acid	<chem>O=C(O)c1cccc(c1)C(=O)O</chem>
9	10.71	3-(4-hydroxyphenyl)-2-hydroxypropanoic acid	<chem>OC(=O)C(O)Cc1ccc(O)cc1</chem>

where the $\text{H}_2\text{O}_2^{\text{bulk}}$ and RhB^{bulk} are H_2O_2 and RhB in bulk solution, respectively, the $\text{H}_2\text{O}_2^{\text{BL}}$ and RhB^{BL} are H_2O_2 and RhB in boundary layer, respectively, $\text{S}^{\text{interface}}$ is the species on the solid-liquid interface, $\text{SiO}_2\text{-Fe}^{\text{III}}$ and $\text{SiO}_2\text{-Fe}^{\text{II}}$ are the Fe^{III} and Fe^{II} species anchored to the surface of SBA-15, respectively, and $\text{SiO}_2\text{-Fe}^{\text{III}}\text{-H}_2\text{O}_2$ and $\text{SiO}_2\text{-Fe}^{\text{II}}\text{-HO}_2\cdot$ are the intermediates of the reaction, respectively.

4 Conclusions

The dual-function mesoporous material Fe/SBA-15 can be synthesized by incipient wetness impregnation and applied to remove refractory dye RhB in aqueous solutions in the presence of H_2O_2 . The characterization by XRD, N_2 adsorption-desorption, SEM, and TEM showed that Fe species occurs both inside and outside the support pores in the form of $\alpha\text{-Fe}_2\text{O}_3$ crystallites, the

loading of Fe in SBA-15 results in the reduced specific area, pore volume, and pore diameter, and Fe/SBA-15 presents the aggregate of rod-like crystallites with a mean diameter of 0.6 μm . The optimum operation conditions at 21 $^{\circ}\text{C}$ for 14 h in Fe/SBA-15- H_2O_2 -RhB system are Fe/SBA-15 dosage at 0.15 $\text{g}\cdot\text{L}^{-1}$, molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ at 2000:1, initial RhB concentration at 10.0 $\text{mg}\cdot\text{L}^{-1}$, and initial solution pH at 5.4 (unadjusted), with approximately 93% RhB removal achieved under the conditions. The adsorption quantity of Fe/SBA-15 acquired from Langmuir isotherm indicates its strong adsorption capacity, which plays an important role in RhB removal from aqueous solutions. Furthermore, the Fe/SBA-15 recovered by H_2O_2 soaking technique is capable of maintaining the catalytic performance during six recycled runs, with RhB removal of approximately 80% and Fe leaching less than 0.1 $\text{mg}\cdot\text{L}^{-1}$ (leaching mass fraction less than 0.6%) for each run. The removal pathway and degradation products of RhB could be determined by UV-Vis absorption spectra and GC-MS analyses. The removal mechanism can be proposed as surface adsorption and Fenton oxidation.

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