



Natural graphite tailings as heterogeneous Fenton catalyst for the decolorization of rhodamine B

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HIGHLIGHTS

- ▶ Graphite tailing was successfully used in the treatment of rhodamine B.
- ▶ Single adsorption and heterogeneous Fenton of graphite tailing were compared.
- ▶ Graphite tailing was novelty both adsorbent and initiator of heterogeneous Fenton.
- ▶ The reactions of rhodamine B obeyed the pseudo-first order kinetics.

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ABSTRACT

A heterogeneous Fenton decolorization process of rhodamine B in aqueous solution promoted by graphite tailing (GT) was developed. For the first time, GT was used as an initiator for the Fenton reaction. The GT used in this study was characterized by X-ray diffraction (XRD), energy dispersive spectrometry (EDS) and Brunauer–Emmett–Teller (BET) method. The mesoporous structure of the GT made it as an adsorbent and the encapsulated Fe₂O₃ in GT was able to initiate the Fenton reaction. The effects of the initial concentration of the dye, the initial concentration of H₂O₂, catalyst dosage, reaction temperature, stirring speed, particle size of catalyst and the pH value were determined. The results showed that the increase of catalyst dosage, initial concentration of H₂O₂, reaction temperature and stirring speed favor the increase of decolorization rate. The increase of initial concentration of the dye and the particle size of catalyst lead to the decrease of decolorization rate and the optimum pH was the original pH of rhodamine B solution. Under the optimal condition, the decolorization and TOC removal rates were 93.39% and 49.02% respectively after 240 min treatment. The release of the iron ion from GT is very little and the intermediates of rhodamine B degradation will not cause the wavelength shift of rhodamine B. The kinetic results showed that the decolorization and degradation of rhodamine B obeyed the pseudo-first order equation.

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1. Introduction

Dyes wastewater has become one of the major environmental problems in the world, because of their coloring, toxicity and non-biodegradable characteristics. It is estimated that the global consumption of dyes is over 10,000 ton every year, and about 10% is discharged without any industrial treatment, for the lacking of effective technology or the high cost of treatment [1,2]. To remove dye pollutants in wastewater, many traditional physical methods have been used, such as adsorption on activated carbon, coagulation

by chemical agent and reverse osmosis [3–6]. However, these methods are non-destructive to dye structure and merely transfer contaminants from water to sludge, which may cause the secondary pollution [7].

In order to develop an efficient method to degrade the dyes, whose structure is much stable since most of them is aromatic compounds, advanced oxidation processes have been widely used in recent years. Especially, Fenton processes have been proved as one of the best methods for the destruction of organic pollution, which involve the generation of highly oxidative hydroxyl radical [8,9]. However, the homogeneous Fenton process has a distinct shortcoming that the resulting concentration of iron ion is much greater than the international effluent standard of wastewater, causing a secondary pollution, and the following removal of iron

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ion makes the process laborious and non-economical [10,11]. On the other hand, to avoid the iron pollution, many researchers try to prepare heterogeneous catalysts by loading iron-containing compounds onto insoluble supports, such as saponite clay [12], carbon [13], kaolin [14], zeolite [15] and silica [16]. Although these heterogeneous catalysts are effective, these methods usually suffer from complex and demanding synthetic processes, such as calcinations at high temperature. It seems that a cheap and readily available heterogeneous catalyst will be a good choice for the degradation of dyes.

Graphite tailing (GT) is a waste after the extraction of graphite mineral. To the best of our knowledge, it has been only used as the building material to produce brick and cement before this study. We notice that the GT containing iron oxides may be a naturally iron-immobilized catalyst for the Fenton process. Furthermore, the mesoporous structure of GT would be able to improve the rate of oxidation by absorbing the organic pollutants, which should make the access to oxidative species much easier. In short, these characters may render graphite tailing an efficient and cost-effective catalyst for wastewater treatment.

Rhodamine B is an important dye and is widely used in textile industry. However, rhodamine B has been corroborated as carcinogen and teratogenic agent, especially for pregnant women and children [17]. Therefore, its removal from wastewater is of significance. The purpose of this study is to investigate the using of GT, a cheap industry waste, in heterogeneous Fenton process for decolorization and degradation of rhodamine B aqueous solution. The effect of each reagent was discussed and reaction parameters in heterogeneous Fenton process were evaluated, such as catalyst dosage, pH, initial concentration of dye solution and H_2O_2 . The decolorization process of rhodamine B was analyzed by UV–VIS spectra at 300–800 nm. The decolorization and degradation kinetics were investigated and the data obeyed the pseudo-first order equation.

2. Materials and methods

2.1. Materials

All chemicals used here were analytical grade and without further purification. Rhodamine B was supplied by Shanghai Chemical reagent Ltd. Co. (Shanghai, China). H_2O_2 (30 wt.%) was supplied by Sinopharm Chemical reagent Ltd. Co (Shanghai, China). The solution pH was adjusted by using 0.1 M HCl or NaOH aqueous solution. Distilled water was used throughout the experiments. The molecular structure of the dye is shown in Fig. 1. The graphite tailing was obtained from graphite processing plant in Qingdao, China. The GT was dried at ambient temperature for a week and stored in a sealed plastic bag for further test. The particle size analysis of graphite tailing was investigated using 40 and 60 mesh filter screens, and the weight percent of GT which was greater than

350 μm , during 245–350 μm and less than 245 μm were 12.97%, 68.84% and 18.19%, respectively.

2.2. Experimental procedures

All experiments were conducted in a conical flask (250 mL) placed in a constant temperature shaker. The 100 mL of rhodamine B solution (100 mg/L), certain amount of GT and H_2O_2 was added into conical flask, respectively. The conical flask was then sealed with parafilm and shaken in the shaker. The temperature and the rotation speed of constant temperature shaker were 30 °C and 180r/min, respectively. Reaction mixture samples (1 mL) were taken at given time intervals and 10 μL 1 M *n*-butanol was then immediately added as the hydroxyl radical scavenger to quench the reaction [18]. The resulting mixture was then filtered through 0.45 μm filter membrane to remove catalyst particles and analyzed using a UV–VIS spectrophotometer immediately.

2.3. Analytical methods

The pH value of the solutions was measured by a digital pH meter (Sartorius, Germany). The UV–VIS absorption spectra of rhodamine B were recorded from 300 to 800 nm using a Cary 50 UV–VIS spectrophotometer (Varian, USA), with a spectrometric quartz cell (1 cm path length), and the maximum absorption wavelength (λ_{max}) of rhodamine B was confirmed as 554 nm. A calibration curve was obtained by measuring the absorbance of different concentration rhodamine B aqueous solution at the maximum absorption wavelength (554 nm) and the reaction mixture samples should be diluted with distilled water when the absorbance exceeded the range of calibration curve. Therefore, the concentration of rhodamine B in the reaction mixture at different reaction time was measured by the absorption intensity at $\lambda_{\text{max}} = 554 \text{ nm}$. In order to evaluate the possibility of the absorption wavelength shift caused by intermediates, the purchasing intermediates were mixed with rhodamine B one by one, at the same mole concentration as the pure rhodamine B aqueous solution, and the UV–VIS absorption spectra of the mixture were detected from 300 to 800 nm. The mineral composition of GT was analyzed with X-ray powder diffraction (XRD) using Cu K α radiation on a D8 Advance X-ray diffractometer (Bruker, Germany) and operated in the condition of 40 kV, 40 mA and 5–95°. The surface area of GT was measured by BET method (Brunauer–Emmett–Teller) with APAS 2020 (Micromeritics, USA) by adsorption/desorption of nitrogen at 77 K and the sample was degassed at 250 °C for 6 h prior to test. The energy dispersive spectrometry (EDS) was performed to determine the chemical composition in the GT using the S-4800 scanning electron microscope (SEM) (Hitachi, Japan). Total organic carbon was determined using liquid TOC II (Elementar, German) to evaluate the degree of mineralization of rhodamine B dye. The iron ion concentration in the aqueous solution was determined using Atomic Absorption Spectrophotometer (AAS) model AA6650 (Shimadzu, Japan) at 248.33 nm, the maximum absorption wavelength (λ_{max}) of iron ion.

3. Results and discussion

3.1. Catalyst characterization

The chemical elements of GT were analyzed and the results (Table 1) showed that the main elements of the catalyst were Si and O. This is in accord with the XRD patterns that the main support material was silicon dioxide. The catalytic material-iron had certain proportion in the catalyst. The weight percentage and atomic percentage of Fe element were 15.00% and 6.26% respectively. This is higher than the reported heterogeneous Fenton catalysts such as

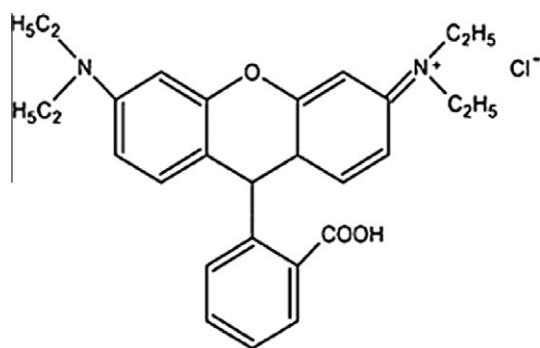
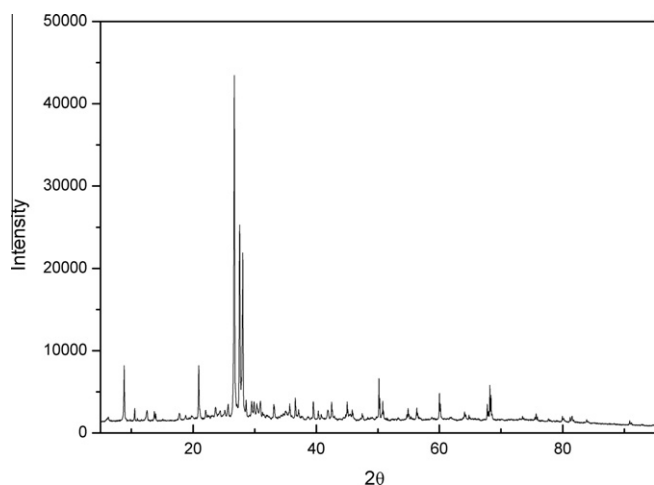
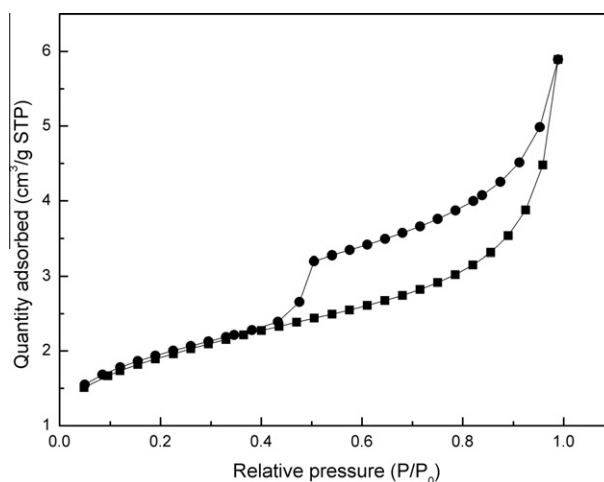


Fig. 1. Molecular structure of Rhodamine B.

Table 1

Energy dispersive spectrometry (EDS) analysis of GT.

Element	Weight percentage (wt.%)	Atomic percentage (at.%)	Element	Weight percentage (wt.%)	Atomic percentage (at.%)
O	40.12	58.41	K	3.73	2.22
Mg	3.61	3.46	Ca	6.79	3.94
Al	5.92	5.11	Fe	15.00	6.26
Si	24.84	20.60			

**Fig. 2.** XRD pattern of GT.**Fig. 3.** N₂ adsorption/desorption isotherms of GT at 77 K.

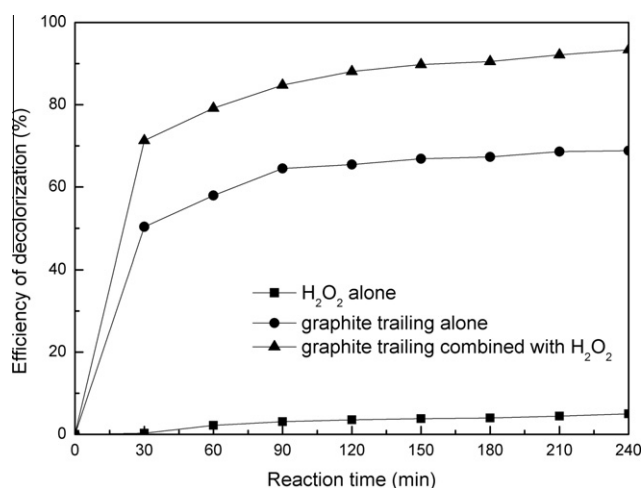
loading the iron salt on the vermiculite and NaY zeolite [8,19]. The EDS analysis confirmed that the catalyst contains iron element and it may serve as an initiator of Fenton reaction.

The XRD spectrum was analyzed to evaluate the chemical component of GT in Fig. 2. The main diffraction peaks were the typical diffraction peaks for the silicon dioxide, so the main support material of the catalyst was confirmed. The XRD pattern of the corresponding Fe-catalyst showed the diffraction peak at $2\theta = 26.78^\circ$, 27.72° , 32.93° , 39.40° , 54.94° and 60.02° that were assigned to (120), (112), (122), (123), (004), (021) planes of Fe_2O_3 respectively. Other weak peaks on the spectrum were the diffraction peaks of other silicates.

Fig. 3 was the nitrogen adsorption and desorption isotherm of GT, which was the type IV isotherm. Based on the isotherm, the textural properties of GT were calculated. The BET surface area, pore volume and pore size were $9.945 \text{ m}^2/\text{g}$, $0.08485 \text{ cm}^3/\text{g}$ and 6.6992 nm , respectively. The properties of GT were favorable for the adsorption of pollutants.

3.2. Decolorization effect comparison of GT alone, H_2O_2 alone and GT combined with H_2O_2

To investigate the effect of every reagent, batch experiments were conducted to contrast the decolorization effect by H_2O_2 alone, GT alone and GT combined with H_2O_2 . Fig. 4 showed a small change of rhodamine B concentration after 240 min treatment by H_2O_2 alone and the decolorization of rhodamine B is only 4.98%. Two reasons possibly can explain this phenomenon. First, the oxidizing power ($E_0 = 1.78 \text{ V}$) of hydrogen peroxide may be not enough for direct oxidation of rhodamine B [20]. Second, the hydroxyl radical ($E_0 = 2.85 \text{ V}$), which is a greater oxidant and can oxidize most organic compounds, cannot be efficiently formed in the absence of the catalyst. This result is in agreement with the literature [21]. For the direct adsorption process using GT, the decolorization rate is 68.83%. This is due to the mesoporous structure of GT and there is great specific area and poriness, which render it the

**Fig. 4.** Effect of GT alone, H_2O_2 alone and GT combined with H_2O_2 on decolorization of rhodamine B. $[\text{RhB}] = 100 \text{ mg/L}$, GT dosage = 50 g/L , $[\text{H}_2\text{O}_2] = 10 \text{ g/L}$, $\text{pH} = 3.92$, reaction temperature = 30°C , stirring speed = 180 r/min , the particle size $< 350 \mu\text{m}$.

capability to adsorb the dye. For the GT and hydrogen peroxide combination system, the efficiency of decolorization was 93.39%. Such an enhancement in color removal may be ascribed to the synergy of adsorption by GT and heterogeneous Fenton oxidation reaction catalyzed by GT. From all of the above results, a picture of the reaction process with the combination reagent may be drawn. Rhodamine B was absorbed onto GT and the oxidant H_2O_2 was then added, which was transferred to the active oxygen species hydroxyl radicals, under the catalysis of encapsulated Fe_2O_3 . The rhodamine B molecular was then degraded by hydroxyl radicals and the adsorbed molecular will have more chance to be oxidized than the molecular in solution, since they was in good interaction with the encapsulated Fe_2O_3 , which is the center of hydroxyl radicals produced.

3.3. Effect of reaction parameters on the decolorization of rhodamine B

3.3.1. Effect of the initial concentration of rhodamine B

The effect of the initial concentration of rhodamine B on the dye decolorization by heterogeneous Fenton was investigated in the range from 50 to 200 mg/L. The results are showed in Fig. 5. Among the four initial rhodamine B concentrations, a higher initial concentration of the dye led to lower decolorization when other reaction conditions were constant. After a treatment for 240 min, the decolorization rate range from 97.53% to 59.93% when the initial concentration of rhodamine B varied from 50 mg/L to 200 mg/L. This behavior is characteristic of advanced oxidation processes [22]. In the same catalyst dosage condition, the increase of rhodamine B concentration resulted in the saturation of GT and the decrease of degradation rate, since the maximum absorption ability and the reaction center of GT is constant [23]. The other reason is that in the same concentration of hydrogen peroxide, the amount of HO \cdot radicals in the reaction system would be constant under the same conditions. The higher concentration of rhodamine B would consume more HO \cdot radical, so the effect would be reduced with the increase of the initial concentration of rhodamine B [24,25]. In addition, the non-specific oxidation of major intermediates with hydroxyl radicals may lead to the side reactions and the competitive consumption of hydroxyl radicals [26].

3.3.2. Effect of catalyst dosage

Catalyst dosage markedly influences heterogeneous Fenton reactions [27]. Therefore, a series of experiments were carried out to investigate the influence of catalyst dosage on the decolorization of rhodamine B, by varying the amount of GT from 10 g/L to 60 g/L. The results were shown in Fig. 6. The decolorization increased from 51.05% to 93.39% with the increase of catalyst from 10 g/L to 50 g/L and the decolorization increased slightly when the GT dosage increase from 50 g/L to 60 g/L after 240 min treatment. This phenomenon is simply due to the fact that the increase of the amount of active sites on GT accelerates the formation of free hydroxyl radical [28]. Hydroxyl radical can efficiently attack the chromophore, thus increasing the decolorization rate of rhodamine B [29].

3.3.3. Effect of H₂O₂ concentration

The concentration of hydrogen peroxide is an important parameter in Fenton reaction process. The effect of hydrogen peroxide

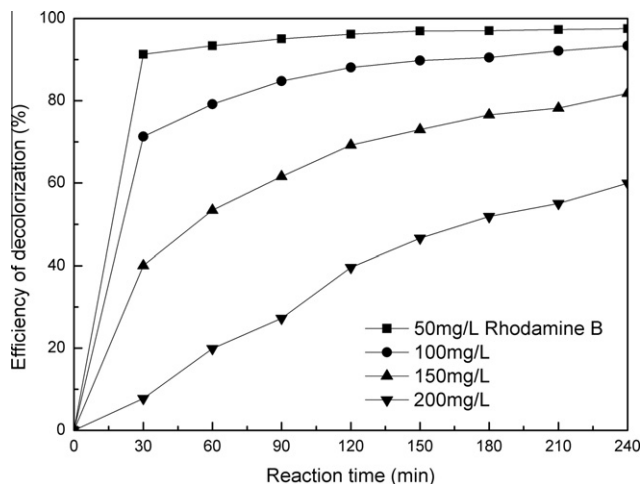


Fig. 5. Effect of initial concentration of rhodamine B on decolorization of rhodamine B. GT dosage = 50 g/L, [H₂O₂] = 10 g/L, pH = 3.92, reaction temperature = 30 °C, stirring speed = 180 r/min, the particle size <350 μ m.

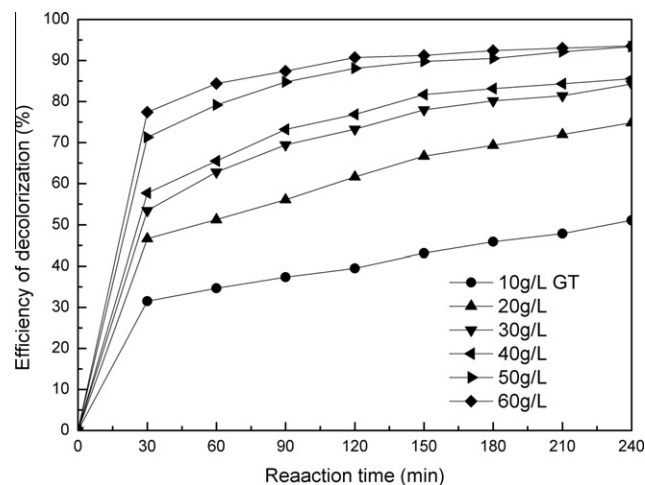


Fig. 6. Effect of catalyst dosage on decolorization of rhodamine B. [RhB] = 100 mg/L, [H₂O₂] = 10 g/L, pH = 3.92, reaction temperature = 30 °C, stirring speed = 180 r/min, the particle size <350 μ m.

concentration on dye decolorization within the range from 5 g/L to 25 g/L was investigated and the results were shown in Fig. 7. The decolorization increased from 85.07% to 93.39% with the increase of hydrogen peroxide concentration from 5 g/L to 10 g/L. This is due to hydrogen peroxide was decomposed at the surface of encapsulated Fe₂O₃ to generate hydroxyl radicals. High concentration of hydrogen peroxide can produce more hydroxyl radical. Nevertheless, when hydrogen peroxide concentration was varied from 15 g/L to 20 g/L, there was no significant variation on the color removal and the decolorization increased only from 93.61% to 94.43%. Higher concentration of hydrogen peroxide cannot distinctly increase decolorization rate because excess of hydrogen peroxide reacts with hydroxyl radical to generate perhydroxy radical which is a scavenger of hydroxyl radical and the oxidation is lower [30]. The reaction was expressed by the follow equation [31]:



3.3.4. Effect of pH

It is known that pH plays an important role in Fenton process. To investigate the influence on the decolorization of rhodamine B

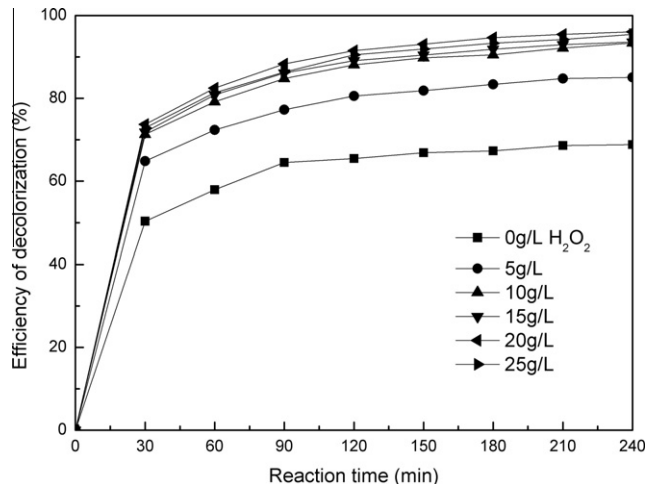


Fig. 7. Effect of initial concentration of H₂O₂ on decolorization of rhodamine B. [RhB] = 100 mg/L, GT dosage = 50 g/L, pH = 3.92, reaction temperature = 30 °C, stirring speed = 180 r/min, the particle size <350 μ m.

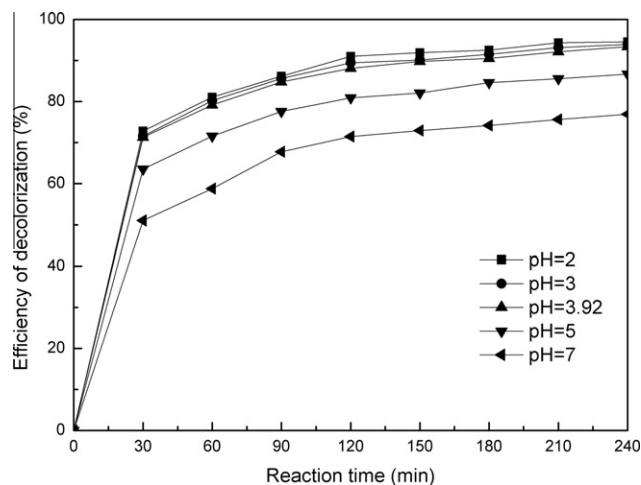


Fig. 8. Effect of pH on decolorization of rhodamine B. [RhB] = 100 mg/L, GT dosage = 50 g/L, $[H_2O_2]$ = 10 g/L, reaction temperature = 30 °C, stirring speed = 180 r/min, the particle size <350 μ m.

in heterogeneous Fenton reaction, the dye solution was adjust to the desired pH from 2 to 7 by adding sodium hydroxide or hydrochloric acid. Fig. 8 showed that the variations of decolorization rate of dye was slightly from pH = 2 to pH = 3.92 and the removal rate was 94.57% and 93.39% respectively. However, the removal rate became worse when pH > 3.92. The results are in agreement with the classic Fenton process, in which the oxidization of hydroxyl radical and hydrogen peroxide is higher in acidic medium [7,32]. The decrease of decolorization rate at pH > 3.92 can be ascribed that at higher pH value the hydroxyl peroxide decomposed to produce oxygen [8]. The original pH of the aqueous rhodamine B solution was 3.92 and the decolorization rate arrived to a higher datum (93.39%), so it is not necessary to adjust the pH by the buffer solution.

3.3.5. Effect of reaction temperature

The effect of reaction temperature on the dye decolorization by heterogeneous Fenton was investigated between 20 °C and 50 °C. Fig. 9 showed that the reaction temperature had positive effect on the decolorization of rhodamine B. The decolorization increased from 84.58% to 93.39% with the increase of reaction temperature from 20 °C to 30 °C and the decolorization increased slightly when reaction temperature increase from 30 °C to 50 °C after 240 min treatment. This is because higher temperature increased the reaction rate between hydroxyl peroxide and catalyst, and the generation rate of hydroxyl radical increased simultaneously [1,33].

3.3.6. Effect of stirring speed

To study the effect of the string speed on the decolorization of rhodamine B, the reactions were conducted from 120 r/min to 210 r/min. Fig. 10 showed that an increase of stirring speed from 120 r/min to 180 r/min improved the decolorization from 86.08% to 93.39% after 240 min reaction and when the stirring speed was higher than 180 r/min, the decolorization increased very slightly. It was due to the fact that the mixture was more homogeneous in the high stirring speed and the higher stirring speed increased the contact chance of reaction system with rodamine B molecule.

3.3.7. Effect of particle size

The influence of the particle size on the dye decolorization of rhodamine B by heterogeneous Fenton was investigated using GT which was greater than 350 μ m, during 245–350 μ m and less than

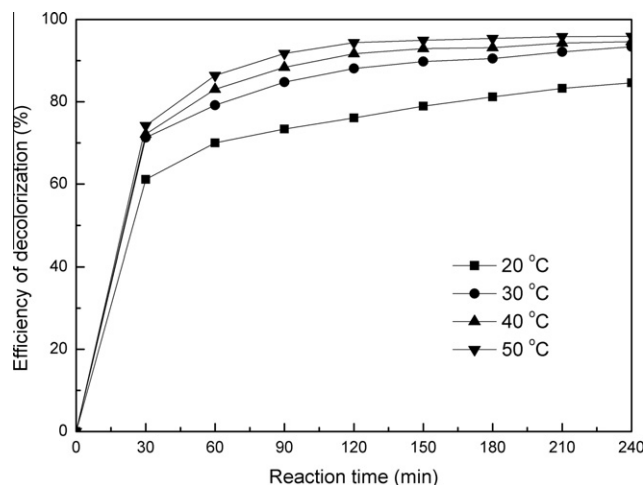


Fig. 9. Effect of reaction temperature on decolorization of rhodamine B. [RhB] = 100 mg/L, GT dosage = 50 g/L, $[H_2O_2]$ = 10 g/L, pH = 3.92, stirring speed = 180 r/min, the particle size <350 μ m.

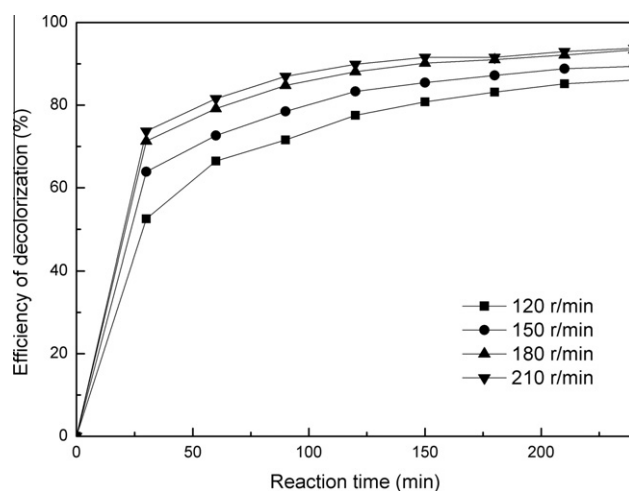


Fig. 10. Effect of stirring speed on decolorization of rhodamine B. [RhB] = 100 mg/L, GT dosage = 50 g/L, $[H_2O_2]$ = 10 g/L, pH = 3.92, reaction temperature = 30 °C, the particle size <350 μ m.

245 μ m, and the decolorization was 68.08%, 92.68% and 95.51% respectively (Fig. 11). The particle size had a certain influence on the decolorization, probably because that the smaller GT particle own a higher specific surface area, which may enhance the adsorption effect and increase the active sites of Fenton reaction. The decolorization was similar when the particle size of GT was during 245–350 μ m and less than 245 μ m, so the particle size which was less than 350 μ m was used through the experiments.

3.4. Mineralization and the reaction kinetics of rhodamine B

It is well known that a better decolorization of rhodamine B does not mean a good mineralization rate of rhodamine B. To investigate the degree of mineralization during the degradation of the rhodamine B by GT in the presence of H_2O_2 , the change of TOC was detected. The TOC removal rate is calculated as below:

$$\text{TOC removal (\%)} = [(TOC_0 - TOC_t) / TOC_0] \times 100 \quad (2)$$

where TOC_0 is the initial TOC of rhodamine B solution and TOC_t is the TOC of rhodamine B aqueous solution at time t , and t is the degradation time. As shown in Fig. 12, the TOC removal rate was

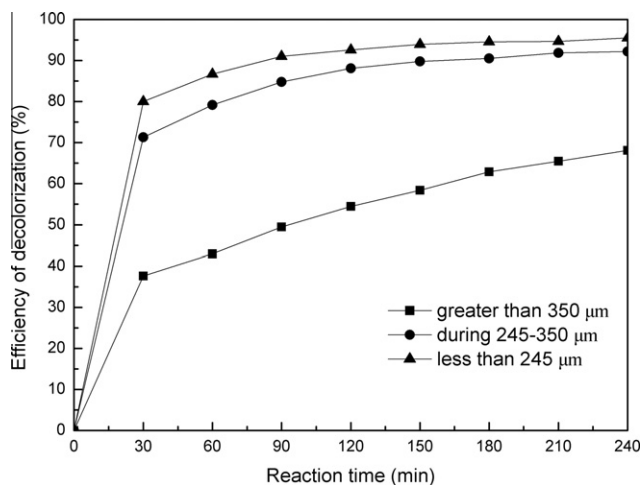


Fig. 11. Effect of particle size of catalyst on decolorization of rhodamine B. [RhB] = 100 mg/L, GT dosage = 50 g/L, $[H_2O_2]$ = 10 g/L, pH = 3.92, reaction temperature = 30 °C, stirring speed = 180 r/min.

lower than the corresponding decolorization rate. When the decolorization of dye was 93.39%, the TOC removal rate was only 49.02%. The difference of decolorization and TOC removal rate of dyes had been well documented in literatures [34–36]. The chromophore of dye was destructed, but the organic pollutant was only partly oxidized to CO_2 and H_2O and the intermediates of degradation contributed to the TOC value.

The degradation and decolorization kinetics of rhodamine B in aqueous solution were investigated, using GT heterogeneous Fenton process under optimum conditions. The pseudo-first-order kinetic equation was employed to investigate the effect of reaction in the heterogeneous Fenton processes.

$$\ln(C_0/C) = kt \quad (3)$$

where C_0 is the initial concentration of rhodamine B and C is the concentration of rhodamine B at time t , k is the degradation rate constant, and t is the degradation time. The calculated kinetic parameters of degradation and decolorization of rhodamine B are listed in Table 2.

From Table 2, it is shown that the R ($R = 0.9860$ and 0.9914) values were close to 1 and the decolorization and degradation of rhodamine B all obeyed the pseudo-first order kinetics. The rate constant of decolorization is higher than that of degradation, which

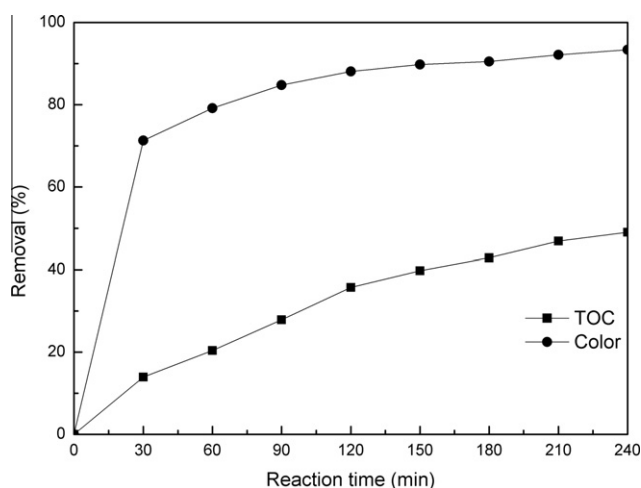


Fig. 12. TOC removal and decolorization of rhodamine B.

means that the rate of decolorization is faster than the rate of TOC removal. This trend is in line with the discussion of decolorization and TOC removal of rhodamine B in the previous section.

3.5. The UV–VIS absorption spectra analysis

In order to investigate the adsorption process with GT and structural change of rhodamine B in heterogeneous Fenton process, the UV–VIS absorption spectra of the dye solution in different reaction times were recorded and shown in Fig. 13. It is shown that the rhodamine B aqueous solution has two characteristic absorption bands, 554 nm and 350 nm. The maximum absorption band is in the visible region, the peak at 554 nm, which should be attributed to the $n \rightarrow \pi^*$ electron transition, and the subordinate absorption band is at 350 nm in the ultraviolet region, which is due to the benzene ring structure of rhodamine B [37]. Under the single action of GT (Fig. 13a), the weakening of absorbing peak at 554 nm reflects that parts of the rhodamine B had been adsorbed by GT. Under the combination effect of GT and H_2O_2 , the absorption peak at 554 nm became weaker along with the increase of reaction time and nearly disappeared after 240 min (Fig. 13b), which indicated that the chromophore, conjugated π system, was destroyed [38]. During the reaction process, no new absorbing band could be found between 300 nm and 800 nm, which indicated that the reaction intermediates have no conjugated π system and no new chromophore formed during the reaction process. Depending on our early research and other literatures, possible intermediates formed from rhodamine B degradation include formic acid, acetic acid, benzoic acid, N,N-diethylaniline, N,N-diethylformamide and N-ethylmaleimide in Fenton reactions [39–41]. In order to clarify the possible wavelength shift effect of intermediates, the interaction experiments between intermediates and rhodamine B was studied. Each intermediate was mixed with rhodamine B one by one and the UV–VIS absorption spectra of the mixture were measured. The results are that the absorption peak at 554 nm and 350 nm of mixture is the same with that of the pure rhodamine B solution, at the same mole concentration. No absorption wavelength shift and no new absorption peak could be found.

3.6. Leaching test and suggested mechanism

In order to evaluate the potential loss of iron ions from GT, leaching test was carried out. Depending on the results of AAS, the concentration of the iron ion in aqueous solution was about 0.4824 mg/L throughout the degradation process of the rhodamine B and the release of the iron ion from GT to the solution could be ignored [1,7]. So it can be concluded that the Fenton oxidation process is mainly due to the heterogeneous catalysis, not to the leaching iron ions and the encapsulated Fe_2O_3 in GT was the Fenton reaction site. First, hydrogen peroxide molecules were transformed to hydroxyl radicals catalyzed by Fe_2O_3 in GT. Second, rhodamine B molecules were oxidized to intermediates and parts of which were oxidized to CO_2 and H_2O . During the oxidation process, the rhodamine B molecules in solution could be oxidized directly by the hydroxyl radicals dispersing in the solution. On the other side, due to the properties of GT, some of Rhodamine B molecules were first adsorbed into the pores of GT and was then oxidated.

Table 2

Pseudo-first order rate constants for decolorization and degradation of rhodamine B in GT heterogeneous Fenton process.

	K (min^{-1})	R^2	R
Decolorization	0.1898	0.9722	0.9860
Degradation	0.0776	0.9828	0.9914

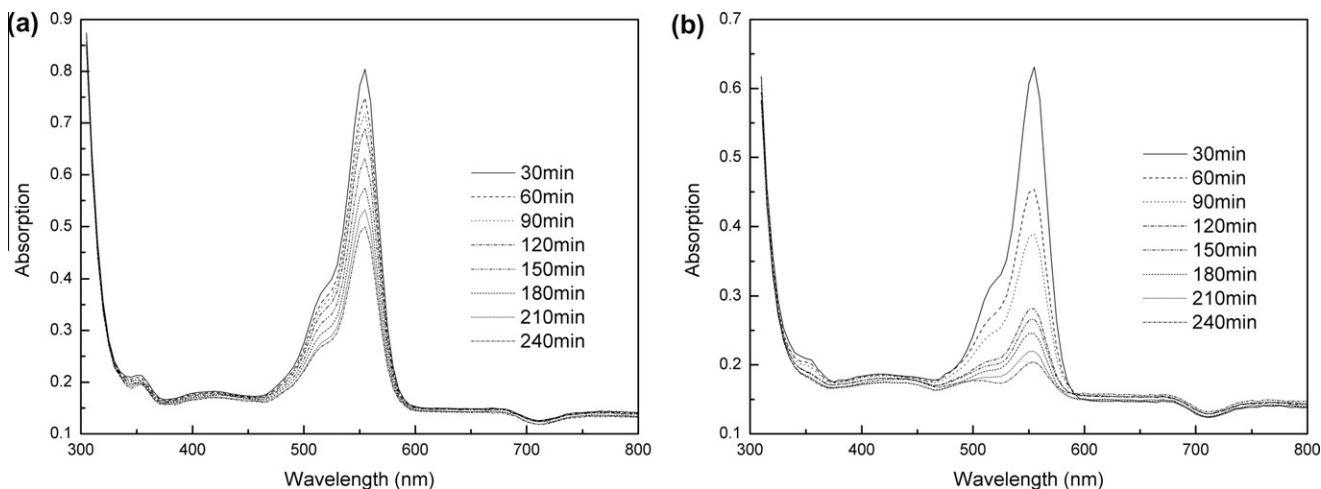


Fig. 13. UV-VIS spectra changes of rhodamine B. (a) GT adsorption process and (b) GT heterogeneous Fenton process.

4. Conclusion

Treatment of rhodamine B in aqueous solution was investigated in a GT promoted heterogeneous Fenton process. The results showed that the increase of catalyst dosage, initial concentration of H_2O_2 , reaction temperature and stirring speed favor the increase of decolorization rate. The increase of initial concentration of the dye and the particle size of catalyst lead to the decrease of decolorization rate and the optimum pH was the original pH of rhodamine B solution. Optimum parameters were obtained: catalyst dosage = 50 g/L, initial concentration of H_2O_2 = 10 g/L, pH = 3.92 (not adjust), reaction temperature = 30 °C, the stirring speed = 180 r/min, the particle size <350 μ m. Under the optimum condition, the decolorization and TOC removal rate was 93.39% and 49.02% respectively. Based on the UV-VIS spectra, GT has two important functions, the adsorption and catalysis effect, and the heterogeneous Fenton process is the combination of them. The release of the iron ion from GT is very little and the intermediates of rhodamine B degradation will not cause the wavelength shift of rhodamine B. The decolorization and degradation reaction of rhodamine B obeyed the pseudo-first order kinetics in this GT promoted heterogeneous Fenton process. In summary, the current process provides an alternative economical method. The scaled-up process of this degradation reaction using GT is now underway in this lab and will be reported in due course.

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