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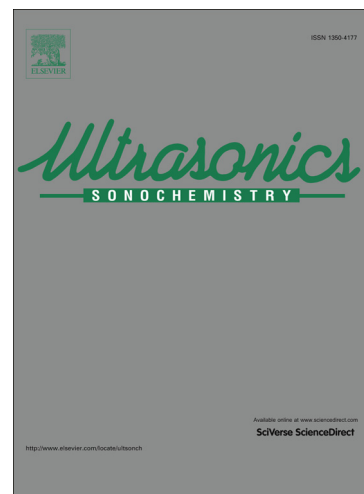
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Sonocatalytic degradation of Rhodamine B catalyzed by β -Bi₂O₃ particles under ultrasonic irradiation

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Abstract

β -Bi₂O₃ particles were synthesized by a polyacrylamide sol-gel method. The sonocatalytic activity of β -Bi₂O₃ particles was evaluated by degrading Rhodamine B (RhB) under the ultrasonic irradiation, revealing that β -Bi₂O₃ particles exhibit a good sonocatalytic activity. The effects of various experimental factors including ultrasonic frequency (f), solution temperature (T), catalyst dosage (C_{catalyst}) and initial RhB concentration (C_{RhB}) on the sonocatalysis efficiency were investigated. The optimum conditions for sonocatalytic degradation of RhB are obtained to be $f = 60$ kHz, $T = 40$ °C, $C_{\text{catalyst}} = 3$ g·L⁻¹, and $C_{\text{RhB}} = 5$ mg·L⁻¹. The percentage degradation of RhB after sonocatalysis for 90 min is 98.7%. Detected by the photoluminescence technique that of using terephthalic acid as a probe molecule, Hydroxyl radicals (\bullet OH) are found to be produced on the irradiated by β -Bi₂O₃ particles. Based on the experimental results, \bullet OH radicals are suggested to be the major active species which are responsible for the degradation reaction.

Key words: β -Bi₂O₃ particles; sonocatalytic activity; influencing factors; \bullet OH radicals

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1. Introduction

It is estimated that about 15% of produced dyes in the world are released into the natural environment during their synthesis and processing [1]. The dyes which release in the textile, rubber, plastics and other industries are harmful to environment and human health [2, 3]. Rhodamine B (RhB) is widely used in industrial processes as a basic dye of the xanthene class. But it is toxic, which is capable to cause irritation to the skin, eyes, astrotintestinal tract which is respiratory tract [4]. Therefore, degradation of dyes (i.e. Rhodamine B) is necessary before they were discharged into the natural environment.

In recent years, ultrasonic degradation as one of the advanced oxidation process (AOPs) has been studied and extensively used to treat organic dye effluents [5, 6]. The main mechanism of ultrasonic process is acoustic cavitations, namely, the process of the formation, growth and implosive collapse of gas bubbles in liquids and releasing a mass of energies [7]. Subsequently, many local hot spots with high temperatures (5000 K) and high pressures (1000 atm) are generated for short period of time. Under such extreme conditions, organic compounds are mineralized and water molecules are cleaved to highly reactive free radicals species. These free radicals are also capable of degrading organic compounds [8, 9].

However, the degradation of organic dye pollutants by ultrasonic usually needs long reaction time [10] and has limited efficiency [11]. In order to overcome these drawbacks, the methods of sonocatalytic degradation are developed [12-14]. Sonocatalytic process contains ultrasonic treatment by catalyst application. Application of catalysts with good adsorption ability, in the sonocatalytic process can increase the formation rate of cavitation bubbles by providing additional nuclei and increase the degradation efficiency of dyes [15-17].

Bi_2O_3 is an important metal oxide semiconductor catalyst, which has been identified as a promising visible light photocatalyst [18, 19]. It has been used in the degradation of organic dyes

due to its chemical structure, non-toxicity, optical and electrical properties. However, very few reports are available to help know about the performance of Bi_2O_3 particles on the ultrasonic-assisted degradation of organics dyes in previous publications.

In this paper, $\beta\text{-Bi}_2\text{O}_3$ particles as a kind of sonocatalysts were synthesized by a polyacrylamide sol-gel method. Its sonocatalytic activity to degrade Rhodamine B (RhB) was studied. The influences of various experimental factors including ultrasonic frequency, solution temperature, catalyst dosage, initial RhB concentration on the sonocatalysis efficiency were systematically investigated. The major active species which is responsible for the degradation reaction was also examined.

2. Experimental

2.1 Materials

All chemicals used in this work were analytical grade reagents. These chemicals were used without further purification. Bismuth nitrate, citric acid, acrylamide and Rhodamine B were all purchased from Tianjin Kemiou Chemical Reagent Co. LTD. Nitric acid was purchased from Xilong Chemical Industry Co. LTD. The solution was prepared with water purified by a Millipore Milli Q system.

2.2 Synthesis of $\beta\text{-Bi}_2\text{O}_3$ particles nanoparticles

0.01 mol of bismuth nitrate was dissolved in 100 mL aqueous nitric acid solution. Then, 0.02 mol of citric acid and 0.1 mol of acrylamide monomers were added successively. The constant magnetic stirring was used during procedure to produce Homogenous additives solution. The solution was heated at 80°C for 10 min to produce a viscous polyacrylamide gel. The gel was dried at 120°C , calcined at 600°C for 2 h to obtain $\beta\text{-Bi}_2\text{O}_3$ particles.

2.3 Characterization

XRD patterns were obtained using Bruker D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) analyses were conducted on a JEOL

JEM-2010 transmission electron microscope. The UV-vis absorption spectra were recorded using a Hitachi U-2001 UV-vis spectrophotometer. Photoluminescence spectra was operated on a PerkinElmer LS-55 luminescence spectromoter.

2.4 Sonocatalytic activity testing

Sonocatalytic degradation of RhB was investigated in the presence of β - Bi_2O_3 particles using a commercial ultrasonic cleaning machine (BK-240), operating at an ultrasonic frequency of 40 or 60 KHz and output power of 240 W. In a typical process, a certain amount of the catalyst was added to 20 mL RhB aqueous solution in a glass beaker. The obtained solution was magnetically stirred for 30 min in the dark to reach the absorption-desorption equilibrium between the catalyst and RhB, and then submitted to the ultrasonic irradiation. The sonocatalytic experiment was performed in the dark to avoid photoexcitation of β - Bi_2O_3 particles. At the regular time intervals, 3 ml of the irradiated suspensions was withdrawn and centrifuged to remove the catalyst and then, remaining RhB absorption was recorded at RhB maximum absorbance wavelength of 554 nm by a UV-vis spectrophotometer. The degradation efficiency is defined as $(C_0 - C_t)/C_0 \times 100 \%$, where C_0 is the initial concentration of RhB and C_t means the concentration of RhB at distinct process time. During the experiment, the ultrasonic bath temperature was controlled by circulating running water through the ultrasonic bath.

2.4 Hydroxyl radicals ($\bullet\text{OH}$) analysis

By using Terephthalic acid (TPA) as a probe molecule, the photoluminescence (PL) technique was used to examine the $\bullet\text{OH}$ radicals produced by the ultrasonic-irradiated β - Bi_2O_3 catalyst. TPA can readily react with $\bullet\text{OH}$ radicals to produce a highly fluorescent compound, 2-hydroxyterephthalic acid (TAOH). The PL intensity of TAOH at 429 nm is proportional to the amount of produced $\bullet\text{OH}$ radicals. Terephthalic acid was added to sodium hydroxide solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$), to obtain a $2.5 \times 10^{-4} \text{ mol L}^{-1}$ TPA solution. The catalyst was added to the

solution with a concentration of 1.0 g L^{-1} . After magnetically stirred for 30 min in the dark, the mixed solution was placed in the ultrasonic bath for ultrasonic irradiation. The reacted solution was centrifuged to remove the catalyst and analyzed by recording the PL measurements at a luminescence spectrometer with the excitation wavelength of 315 nm.

3. Results and discussion

3.1 The XRD pattern and the TEM image of $\beta\text{-Bi}_2\text{O}_3$ particles

Fig. 1 shows the XRD pattern of $\beta\text{-Bi}_2\text{O}_3$ particles, and the standard diffraction pattern of tetragonal crystal structure of the $\beta\text{-Bi}_2\text{O}_3$ (JCDPS 27-0050). It is seen that all the diffraction peaks are related to the tetragonal $\beta\text{-Bi}_2\text{O}_3$ phase, and no traces of second phase are detected in the XRD pattern. Inserted in Fig. 1 is a TEM image of $\beta\text{-Bi}_2\text{O}_3$ particles. It can be seen that $\beta\text{-Bi}_2\text{O}_3$ particles are relatively uniform and oval in shape with an approximately diameter of 150 nm.

3.2 Effect of ultrasonic frequency on the degradation of RhB

Fig. 2 shows the effect of the ultrasonic frequency on the sonocatalytic degradation of RhB separately at 40 and 60 kHz, at different temperatures for 90 min, where the initial concentration of RhB is $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, the loading of the catalyst is $C_{\text{catalyst}} = 1 \text{ g}\cdot\text{L}^{-1}$. This indicates that the sonocatalysis efficiency at the ultrasonic frequency of 60 kHz is larger than that at 40 kHz at different temperatures. The intensity of temperatures and pressures (or sonoluminescence) produced at higher frequencies is enough to generate electron-hole pairs regarding to $\beta\text{-Bi}_2\text{O}_3$ narrow bandgap energy of 2.37 eV. The main reason for the increased sonocatalysis efficiency at higher frequencies is ascribed to the increase in cavitation. In addition, high frequency ultrasound can greatly enhance the diffusion mass transfer [20], which is beneficial to the sonocatalytic degradation of RhB.

3.3 Effect of temperatures on the degradation of RhB

Fig. 3 shows the sonocatalytic degradation of RhB over $\beta\text{-Bi}_2\text{O}_3$ particles versus of time (t) at

different temperatures under ultrasonic irradiation of 60 kHz, where $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{catalyst}} = 1 \text{ g}\cdot\text{L}^{-1}$. The blank experiment reveals a good stability of RhB under ultrasonic irradiation at 60 kHz without catalyst, which indicates that ultrasonic irradiation alone hardly lead to the degradation of RhB. Combination of ultrasonic irradiation with $\beta\text{-Bi}_2\text{O}_3$ particles (as catalyst) increases RhB degradation significantly, indicating good sonocatalytic activity of $\beta\text{-Bi}_2\text{O}_3$.

The sonocatalytic degradation of RhB is dependent on the solution temperature strongly and increases with the increasing of the solution temperature from 20 to 40 °C. However, further increase in temperature up to 50 °C, decreases the RhB degradation owing to the low absorbability, degassing of the solution and cushioning effect of the vapour in bubbles. These results indicated that there exists an optimum temperature for most catalysts to sonocatalytically degrade organic pollutants. There are similar reports on the temperature-dependent sonocatalytic degradation of dyes in the literature [21]. In the present sonocatalysis experiments, at the optimum temperature of 40 °C, the degradation percentage of RhB after sonocatalysis for 90 min is 95.6% at the operating ultrasonic frequency of 60 kHz.

3.4 Effect of $\beta\text{-Bi}_2\text{O}_3$ concentration on the degradation of RhB

Fig. 4 shows the effect of $\beta\text{-Bi}_2\text{O}_3$ concentration on the sonocatalytic degradation of RhB at the operating ultrasonic frequency of 60 kHz, where $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, $T = 40 \text{ }^\circ\text{C}$. The sonocatalysis efficiency increases with increment of catalyst concentration up to 3 g/L, but declines with further increasing. The optimum loading of $\beta\text{-Bi}_2\text{O}_3$ particles is obtained to be 3 $\text{g}\cdot\text{L}^{-1}$, where the percentage degradation of RhB after sonocatalysis for 90 min is 98.7% at the ultrasonic frequency of 60 kHz. In general, an appropriate increase in catalyst dosage can offer more active sites for sonocatalysis, thus leading to an increase in the degradation. However, after optimum catalyst concentration the active sites number declines due to aggregation phenomenon. Furthermore, excessive dosage of catalyst can possibly reduce the transmission of ultrasound waves and lights near the catalyst surface [22, 23].

3.5 Effect of initial RhB concentration on the degradation of RhB

Fig. 5 shows the effect of initial RhB concentration on its sonocatalytic degradation at ultrasonic frequencies of 60 kHz, where the other experiment parameters are fixed at $T = 40\text{ }^{\circ}\text{C}$ and $C_{\text{catalyst}} = 3\text{ g}\cdot\text{L}^{-1}$. It is seen that the degradation rate of RhB exhibits a decreasing trend with the increase in the initial concentration of RhB. This phenomenon can be ascribed to the increase in the number of dye molecules on the surface of the catalyst with increasing the dye concentration [24]. The increased dye adsorption is expected to reduce the adsorption of $\text{H}_2\text{O}/\text{OH}^-$ onto the catalyst surface, and as a result, $\text{H}_2\text{O}/\text{OH}^-$ is decreasingly available for the reaction with holes to generate $\bullet\text{OH}$ radicals, which are verified to be the main active species in the present sonocatalysis.

3.6 Effect of ethanol on the degradation of RhB

It is known that ethanol can be used as a scavenger of $\bullet\text{OH}$ radicals. By investigating the effect of ethanol on the sonocatalysis efficiency of $\beta\text{-Bi}_2\text{O}_3$ particles toward the RhB degradation, we can clarify the role of $\bullet\text{OH}$ radicals in the photocatalysis. Fig. 6 shows the effect of ethanol (10% of volume ratio) on the degradation of RhB after 90 min of ultrasonic irradiation at 60 kHz ($C_{\text{RhB}} = 5\text{ mg}\cdot\text{L}^{-1}$, $C_{\text{catalyst}} = 3\text{ g}\cdot\text{L}^{-1}$, $T = 40\text{ }^{\circ}\text{C}$). It is found that addition of ethanol to the reaction solution decrease the sonocatalytic degradation of RhB from 98.7% to 8.8% under normal condition. This result implies that ethanol exhibits a substantial suppression on the dye degradation, and hence $\bullet\text{OH}$ radicals are suggested to play an important role in the sonocatalysis.

3.7 The PL spectra of the TPA solution

Figs. 7(a) shows the PL spectra of the TPA solution reacted for different times over the ultrasonic-irradiated $\beta\text{-Bi}_2\text{O}_3$ particles at 60 kHz ($C_{\text{catalyst}} = 3\text{ g}\cdot\text{L}^{-1}$, $T = 40\text{ }^{\circ}\text{C}$). It is seen that the TPA reaction solution shows obvious PL signal centered around 429 nm, and its intensity increases with increasing ultrasonic time. This indicates that $\bullet\text{OH}$ radicals are produced under ultrasonic irradiation in the presence of $\beta\text{-Bi}_2\text{O}_3$ particles. Figs. 7(b) shows the PL spectra of the

TPA solution ultrasonic-irradiated for different times without catalyst at 60 kHz ($T = 40\text{ }^{\circ}\text{C}$). The TPA solution shows a weak PL signal, indicating the production of a small amount of $\bullet\text{OH}$ radicals under the ultrasonic irradiation without any catalyst. It should be noted that the local high temperature and pressure (i.e., hot spots) resulted from the sudden collapse of cavitation bubbles can thermally dissociate water into $\bullet\text{OH}$ radicals [25]. However, the $\bullet\text{OH}$ radicals produced without catalyst can be neglected compared to the process conducting in the presence of $\beta\text{-Bi}_2\text{O}_3$ particles. Figs. 7(c) shows the PL spectra of the TPA solution over the ultrasonic-irradiated $\beta\text{-Bi}_2\text{O}_3$ particles when adding 10% ethanol at 60 kHz ($C_{\text{catalyst}} = 3\text{ g}\cdot\text{L}^{-1}$, $T = 40\text{ }^{\circ}\text{C}$). The PL signal almost disappears, suggesting that $\bullet\text{OH}$ radicals are quenched in the presence of ethanol. As the addition of ethanol simultaneously results in a drastic decrease in the sonocatalysis efficiency, $\bullet\text{OH}$ radicals are therefore suggested to be the dominant active species responsible for the dye degradation.

3.8 Effect of pre-adsorption time on the degradation of RhB

In order to find out the effects of adsorption on catalytic ultrasonic process, pre-adsorption was investigated. As shown in Fig. 8. The degradation efficiency had big differences with different pre-adsorption time followed by ultrasonic irradiation. With 10 min', 20 min' and 30 min' pre-adsorption, the degradation efficiency could reach 55%, 63.2% and 70.1% after 10 min ultrasonic irradiation. With 40 min' and 50 min' pre-adsorption, the degradation efficiency could reach 71.2% and 72.1% after 10 min ultrasonic irradiation. These results indicated that the sonocatalytic degradation of RhB is dependent on the pre-adsorption time and increases with the increasing of the pre-adsorption time from 10 min to 50min. However, further increase in pre-adsorption time up to 30 min, the efficiency was not significantly increased only about 1% with further increasing. So the pre-adsorption time choose 30 min.

3.9 The reusability of $\beta\text{-Bi}_2\text{O}_3$ particles on the degradation of RhB

The reusability of $\beta\text{-Bi}_2\text{O}_3$ particles was tested in the presence of ultrasonic frequency of 60

KHz, solution temperature of 40 °C, sonocatalyst dosage of 3 g·L⁻¹, initial dye concentration of 5 mg·L⁻¹ and reaction time of 90 min. As shown in Fig. 9, after five repeated runs, the decline in decolorization efficiency was insignificant. This fact indicates that β -Bi₂O₃ particles can be used as an effective catalyst for the sonocatalytic degradation of RhB in aqueous solution.

3.10 Possible sonocatalytic mechanism of β -Bi₂O₃ toward degradation of RhB

Fig10 shows a possible sonocatalytic mechanism of β -Bi₂O₃ catalyst towards the degradation of RhB. Perhaps a possible mechanism can be explained by means of heat and light energies, namely “hot spot” and sonoluminescence, coming from ultrasonic irradiation. Ultrasonic irradiation combined with β -Bi₂O₃ samples can generate various active species.

Firstly, the heat energies (hot spot) produced by ultrasonic cavitation in a water medium can pyrolyze H₂O molecules into H• and •OH radicals. Recombination of a small part of hydroxyl radicals generates H₂O₂.

Secondly, the light energies (sonoluminescence) caused by ultrasonic irradiation can excite β -Bi₂O₃ particles to act as photocatalyst and then the photo-generated hole-electron pairs form. The photo-generated holes (h⁺) can directly degraded RhB adsorbed on the surface of β -Bi₂O₃ particles. However, h⁺, firstly react with hydroxyl and then produce the •OH radicals (a kind of major active species responsible for the degradation reaction), which is demonstrated in Fig 6 and Fig 7.

Finally, the •OH radicals, h⁺ and H₂O₂ oxidize RhB to CO₂, H₂O and other mineralization of small molecule compounds.

4. Conclusions

Sphere-like β -Bi₂O₃ particles with an average size of ~150 nm were prepared via a polyacrylamide gel route from the XRD pattern and TEM image of β -Bi₂O₃ particles. The sonocatalytic experiments reveal good sonocatalytic activity of β -Bi₂O₃ particles toward the RhB degradation under ultrasonic irradiation. The sonocatalysis efficiency is shown related closely to

the ultrasonic frequency, solution temperature, catalyst dosage, and initial RhB concentration. The optimum conditions for sonocatalytic degradation of RhB are obtained to be $f = 60$ kHz, $T = 40$ °C, $C_{\text{catalyst}} = 3$ g·L⁻¹, and $C_{\text{RhB}} = 5$ mg·L⁻¹. The percentage degradation of RhB after sonocatalysis for 90 min is 98.7%. The addition of ethanol leads to a substantial suppression of RhB degradation due to •OH radicals consumption. Based on the experimental results, •OH radicals are suggested to be the primary active species in the sonocatalysis.

Acknowledgments

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Figure captions

Fig. 1 XRD pattern of β - Bi_2O_3 particles, and the standard diffraction pattern of tetragonal crystal structure of the β - Bi_2O_3 (JCDPS 27-0050). The insert shows a TEM image of β - Bi_2O_3 particles.

Fig. 2 Effect of the ultrasonic frequency on the sonocatalytic degradation of RhB separately at 40 and 60 kHz, at different temperatures for 90 min, $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{catalyst}} = 1 \text{ g}\cdot\text{L}^{-1}$.

Fig. 3 Sonocatalytic degradation of RhB over β - Bi_2O_3 particles as a function of time (t) at different temperatures under ultrasonic irradiation of 60 kHz, along with the blank experiment result. $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{catalyst}} = 1 \text{ g}\cdot\text{L}^{-1}$.

Fig. 4 Effect of β - Bi_2O_3 concentration on the sonocatalytic degradation of RhB at the ultrasonic frequency of 60 kHz. $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, $T = 40 \text{ }^\circ\text{C}$.

Fig. 5 Effect of initial RhB concentration on its sonocatalytic degradation at ultrasonic frequencies 60 kHz. $T = 40 \text{ }^\circ\text{C}$ and $C_{\text{catalyst}} = 3 \text{ g}\cdot\text{L}^{-1}$.

Fig. 6 Effect of ethanol on the degradation of RhB after 90 min of ultrasonic irradiation at 60 kHz. $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$, $C_{\text{catalyst}} = 3 \text{ g}\cdot\text{L}^{-1}$, $T = 40 \text{ }^\circ\text{C}$.

Fig. 7 PL spectra of the TPA solution ultrasonic-irradiated for different times at $T = 40 \text{ }^\circ\text{C}$, 60 kHz, (a) $C_{\text{catalyst}} = 3 \text{ g}\cdot\text{L}^{-1}$, (b) without catalyst; (c) $C_{\text{catalyst}} = 3 \text{ g}\cdot\text{L}^{-1}$, $V_{\text{ethanol}} = 10\%$.

Fig. 8 Degradation efficiency of RhB in catalytic ultrasonic process with different pre-adsorption time.

Fig. 9 Reusability of the β - Bi_2O_3 particles within five consecutive experimental runs after 90 min. $f = 60 \text{ kHz}$, $T = 40 \text{ }^\circ\text{C}$, $C_{\text{catalyst}} = 3 \text{ g}\cdot\text{L}^{-1}$, and $C_{\text{RhB}} = 5 \text{ mg}\cdot\text{L}^{-1}$.

Fig. 10 Possible sonocatalytic degradation mechanism of β - Bi_2O_3 particles on the degradation of RhB.

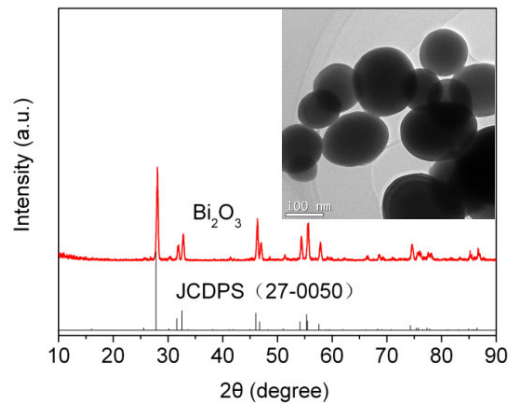


Fig. 1

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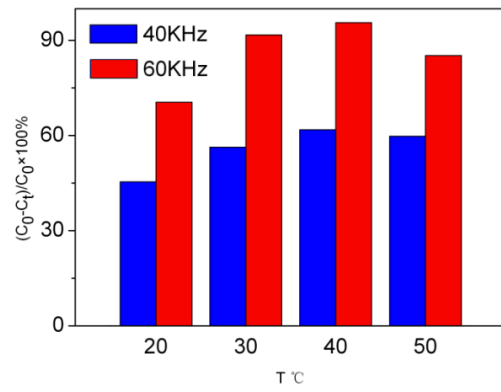


Fig. 2

ACCEPTED MANUSCRIPT

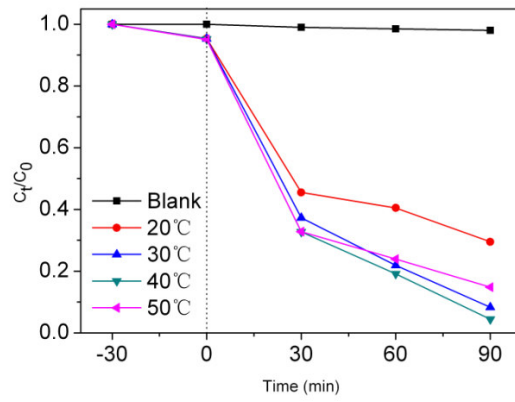


Fig. 3

ACCEPTED MANUSCRIPT

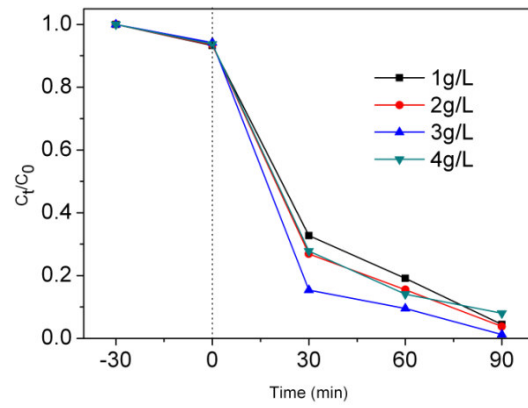


Fig. 4

ACCEPTED MANUSCRIPT

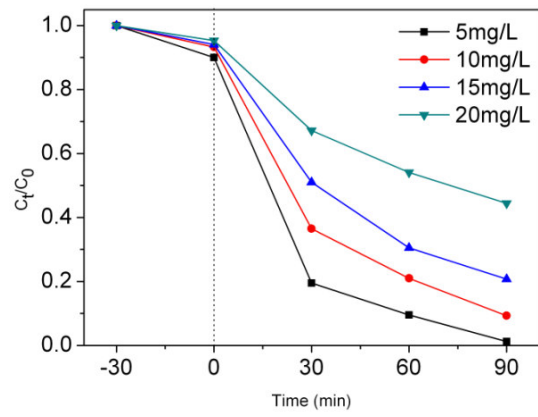


Fig. 5

ACCEPTED MANUSCRIPT

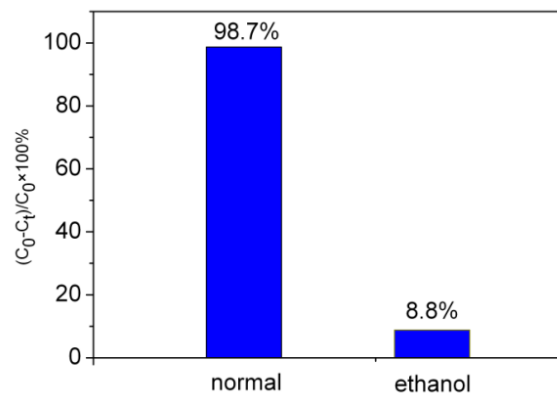


Fig. 6

ACCEPTED MANUSCRIPT

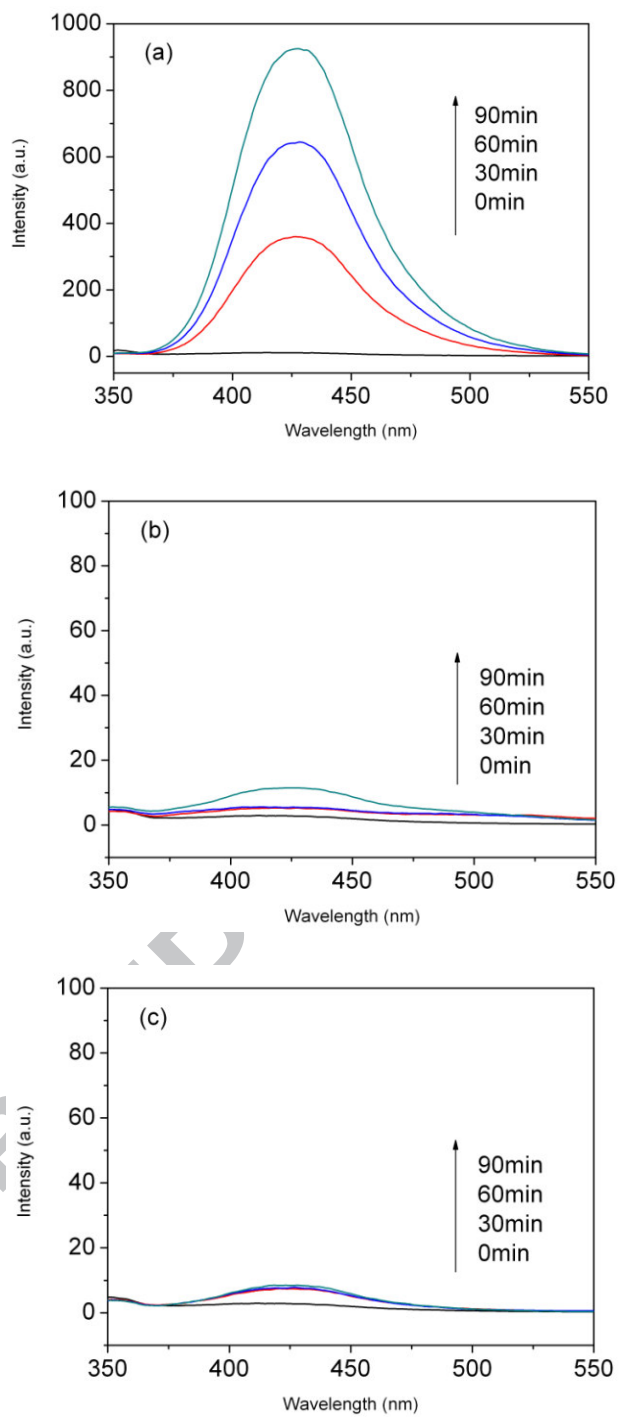


Fig. 7

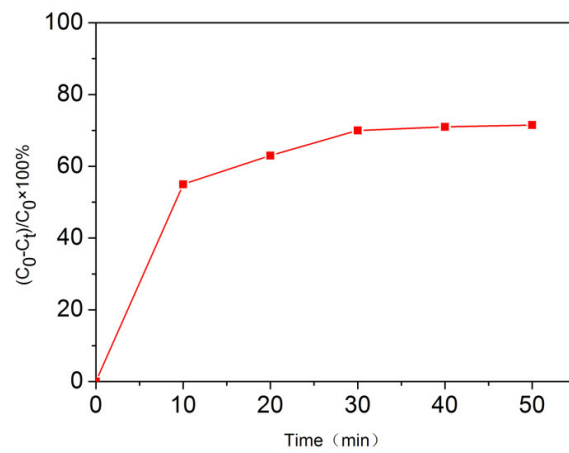


Fig. 8

ACCEPTED MANUSCRIPT

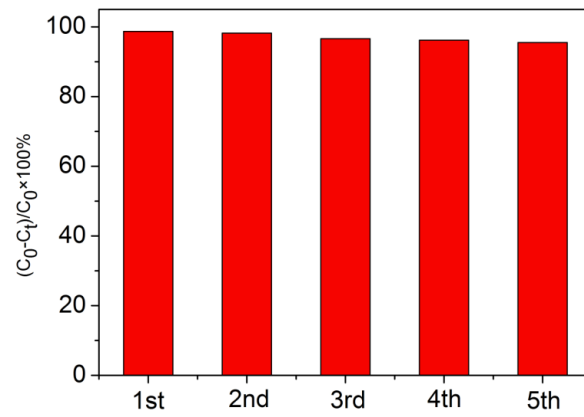


Fig. 9

ACCEPTED MANUSCRIPT

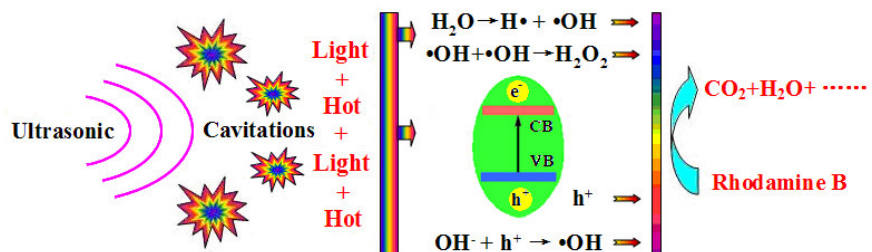


Fig. 10

ACCEPTED MANUSCRIPT