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Highly efficient decomposition of rhodamine B in wastewater with graphene/silver-based nanocomposite catalyst: process optimization and kinetics

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ABSTRACT

The carcinogenicity and reproductive ability of rhodamine B (RhB) towards humans and animals have been proved. Current techniques to treat RhB are non-destructive, high cost and low efficient. Therefore, it has practical significance to establish a reasonable method for effective degradation of RhB. Here, the silica gel (SG)/reduced graphene oxide (RGO)/Ag nanoparticles (Ag NPs) composite as the catalyst for degradation of RhB was facilely prepared. Effect of various parameters on the degradation efficiency of the composite was discussed in detail. Interestingly, the degradation efficiency of RhB can be dramatically improved in the presence of the SG/RGO/Ag composite. Moreover, the degradation efficiency was sensitive to the parameters such as the content of Ag in the composite, $NaBH_4$ dosage, pH value of the solution, the amount of the composite, initial concentration of RhB, temperature and inorganic salts. Under optimal conditions, the degradation efficiency for RhB could reach 100% within 50 s even the content of Ag was only 0.78%, instead of the traditional catalyst with high loading of Ag and low catalytic efficiency. Also, the composite was of low cost, highly stable performance and facile recovery, which is a potential candidate for the catalytic degradation of organic dyes in wastewater treatment.

Keywords: Reduced graphene oxide; Nanocomposite; Structure and performance; Catalysis; Wastewater treatment

1. Introduction

Environmental pollution is a serious problem for the world, such as the discharged dyes and drugs [1]. Especially, the dyes from the textile industry are an important source of environmental contamination. It is estimated that 1%–15% of dyes are discharged into the wastewater [2]. The release of those colored wastewater could affect the photosynthetic reaction in aquatic life, and produce dangerous by-products through oxidation, hydrolysis or other chemical reactions taking place in wastewater [3,4]. Thus, there is a considerable need to treat the colored wastewater before being discharged.

RhB is a highly water soluble, non-volatile, basic dye of the xanthene class, which exhibits high stability in water [5]. The carcinogenicity and reproductive ability towards humans and animals have been proved [6]. A number of conventional treatment methods have been reported for the degradation of RhB, including photodegradation, coagulation, filtration, chemical and biological degradation [7,8]. Even though, these techniques have practical application to some extent, some of them are non-destructive, high cost and low efficient. Therefore, it has practical significance to establish a reasonable method for effective degradation of RhB.

It is reported that dyes can react with $NaBH_4$ under the catalysis of metal-based nanocomposites, and BH_4^- acted as

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electron donors and dyes as electron acceptors [9]. However, reduction of dyes by $NaBH_4$ is very difficult without a catalyst. Several studies have demonstrated that a catalyst with an intermediate redox potential between electron donor and acceptor could facilitate the transfer of electrons, and act as an electron relay [10]. For example, Ag/polystyrene microspheres showed the catalytic activity in the oxidation–reduction reaction of methylene blue contained $NaBH_4$ [11]. Au@TiO_2 nanocomposites were also used in the catalytic degradation of methyl orange and methylene blue in the presence of $NaBH_4$ [12].

As a new kind of carbon materials with two-dimensional cellular structure, graphene exhibits many unique properties, such as huge specific surface area, high mobility of charge carriers, good adsorption capacity and chemical stability. Thus, graphene could be used as a carrier in biological sensors, super capacitor, lithium ion battery and catalytic applications [13]. FeCo nanocrystals encapsulated in N-doped carbon nanospheres/reduced graphene oxide (RGO) can be used as a catalyst, which exhibit markedly enhanced catalytic activity toward the reduction of 4-nitrophenol [14].

The Ag assembled on the surface of the graphene oxide could improve the performance of Ag nanoparticles (Ag NPs) [15]. However, some problems have not been solved yet, such as high loading of Ag NPs, the aggregation of Ag NPs on graphene surface and low catalytic activity. Silica gel (SG) is a common inorganic material with low cost, non-toxic and high stability. Graphene and Ag NPs assembled on the surface of SG, respectively, could effectively prevent Ag NPs and graphene from agglomerating and enhance the performance of the graphene and Ag NPs.

In this paper, a ternary composite, SG/RGO/Ag, is prepared by electrostatic interaction combined with one-step reduction. Its degradation activity for RhB is carried out. Influence of various factors on the catalytic performance of the SG/RGO/Ag composite is investigated in detail.

2. Experimental section

2.1. Materials

Graphite powder with an average size of 30 μm and purity of >95% was obtained from Shanghai Chemical Reagent Co. (Shanghai, China) SG (300–400 mesh) was purchased from Huanghai Chemical Reagent Co. (Shanghai, China) (3-Aminopropyl)triethoxysilane (APTES) was bought from J&K Scientific Ltd. (Shanghai, China) All of the other chemical reagents used in our experiment were of analytical grade, purchased from Shanghai Chemical Reagent Co. and used without further purification. Deionized water was used for all experiments.

2.2. Characterizations

The morphology of the sample was characterized by a JEOL JEM-2100F transmission electron microscope (TEM) (Japan). The TEM samples were prepared by dropping the dispersion of the sample on a carbon-coated copper grid and dried at room temperature. The surface morphology of the sample was observed by a Hitachi S3400N scanning electron microscope (Japan) operated at an accelerating voltage of 15 kV (Japan). X-ray photoelectron spectra (XPS) were carried out on a Thermo ESCALAB 250 X-RAY photoelectron spectrometer with a monochromatic X-ray source (Al Ka hn = 1,486.6 eV) (USA). The energy scale of the spectrometer was calibrated using Au 4f7/2, Cu 2p3/2 and Ag 3d5/2 peak positions. UV-visible spectra were recorded on a UV 1000 spectrophotometer (Japan).

2.3. Preparation of SG/RGO/Ag composites

First, graphite oxide (GO) was obtained using a modified Hummers method [16]. In a typical synthesis of SG/RGO/Ag composites, first, the SG was modified with amino groups as follows: 0.1 mL of APTES was added dropwise into the SG (400 mg) dispersed into isopropanol (20 mL) and heated at 85°C for 2 h. Second, the aminated SG and the GO (2 mL, 1 mg mL^{-1}) were dispersed in deionized water (10 mL) and stirred for 2 h at room temperature. Subsequently, a certain amount of silver nitrate aqueous solution (1 mg mL^{-1}) was added and stirred for another 2 h. Finally, freshly prepared $NaBH_4$ (4 mL, 0.1 mol L^{-1}) was added into the above mixture, and reacted at 90°C for about 6 h. The products (SG/RGO/Ag) with various loading amount of Ag (0.1%, 0.5%, 0.78%, 1% and 1.5%) were obtained by washing with water and dried at 60°C.

2.4. Degradation experiment

In the degradation experiment for RhB, a certain amount of the SG/RGO/Ag was added into the RhB solution with various concentrations (25 mL), respectively. Before introducing $NaBH_4$ (0.05 mol L^{-1}), the mixture of RhB and SG/RGO/Ag was magnetically stirred for 1 h at room temperature in order to establish adsorption/desorption equilibrium. The catalytic activity for the SG/RGO/Ag and the influence of the various factors on the degradation of RhB were evaluated by UV-visible adsorption spectra.

3. Results and discussion

3.1. Morphology and composition of the SG/RGO/Ag composite

As shown in Fig. 1(a), it can be seen that the pure SG has a smooth surface. To study the effect of RGO and Ag NPs on the morphology of the SG, the images of the composite are taken (see Figs. 1(b)–(d)). The results show that the RGO and Ag NPs onto the surface of the SG have a significant influence on the morphology of the SG. Compared with the pure SG (Fig. 1(a)), the SG/RGO/Ag composite has a relatively rough surface (Fig. 1(b)). Obviously, some wrinkles and Ag NPs are observed on the surface of the SG (Fig. 1(c)), and no scattered wrinkles and Ag NPs are observed outside of the SG. High-resolution transmission electron microscopy provides more details about the morphology of the SG/RGO/Ag composite (Fig. 1(d)), the wrinkled, folded sheets and the spherical Ag NPs could be observed clearly. The size of nanoparticles ranges from 10 to 60 nm, and it is focused on 30–40 nm, as illustrated in the inset of Fig. 1(c). Moreover, no obvious aggregation for the wrinkles and black particles is observed in the image.

The evidence about the composition of SG/RGO/Ag was obtained by XPS analysis. As shown in Fig. 2(a), the XPS peaks of Si, C, Ag, N and O could be observed. The Si, C

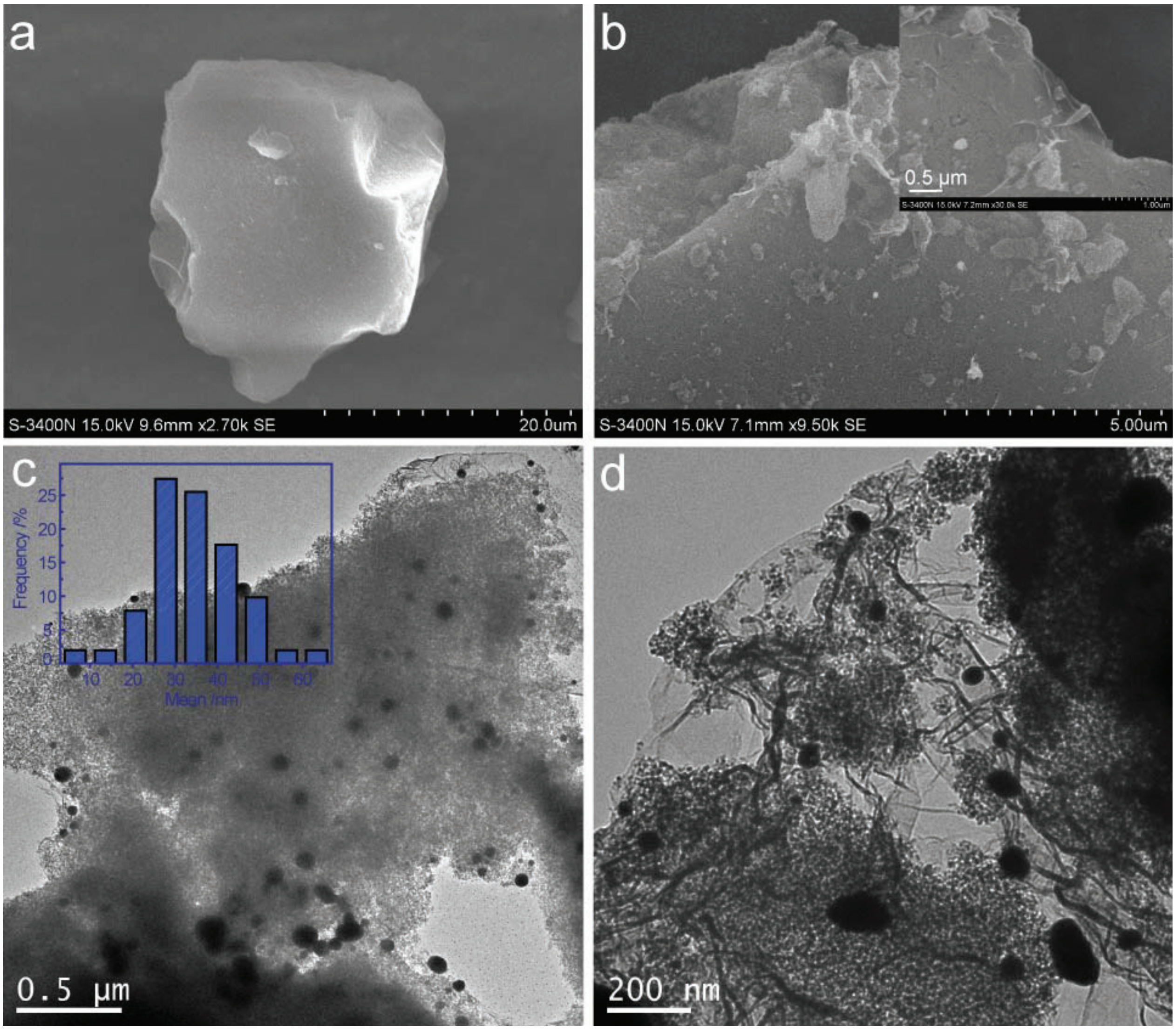

Fig. 1. SEM images of the SG (a) and the SG/RGO/Ag (b). TEM images of the SG/RGO/Ag ((c) and (d)), the inset in (c): size distribution histogram for Ag NPs in the SG/RGO/Ag.

and O come from SG and RGO, the N comes from APTES and the Ag comes from Ag NPs. In order to identify the valence state of Ag in the assembly, the high-resolution XPS of Ag3d is measured. Clearly, the Ag3d bank (Fig. 2(b)) could be divided into four peaks with binding energy at 368.7, 374.7, 367.9 and 373.9 eV, respectively, which indicates that there exists two kinds of Ag on the surface of the composite [17]. The peaks located at 368.7 and 374.7 eV (Fig. 2(b)) are attributed to Ag 3d5/2 and Ag 3d3/2, respectively, suggesting that Ag element is present in the SG/RGO/Ag composite [18]. The peaks of Ag 3d5/2 and Ag 3d3/2 at 367.9 eV and 373.9 eV, respectively, could be caused by the following two reasons: the surface oxidation of Ag or the interaction between Ag NPs and other materials with lower Fermi level [19]. XPS analysis reveals the presence of RGO and Ag NPs in the composite. The RGO and Ag NPs evenly dispersed on the SG (Fig. 1) could provide active sites for the catalytic degradation of RhB, which is beneficial to improve the catalytic activity of the composite.

Moreover, the crystal structure of SG/RGO/Ag and the SG/RGO were characterized by X-ray diffraction (XRD). As shown in Fig. 3, the peak located at about 2θ = 20° belongs to the non-crystalline SiO_2 in the composite. Compared with that of the SG/RGO (Fig. 3(a)), some new peaks at 2θ = 37.7°, 43.9°, 64.2° and 77.1° are observed, which correspond to the reflections of (111), (200), (220) and (311) crystalline planes of the fcc structure of Ag (JCPDS no. 04–0783), respectively. Also, it should be noted that, besides elemental Ag, no other diffraction peaks are observed in the XRD of the SG/RGO/Ag composite, indicating that the abundant species of Ag in the composite are elemental Ag. As a result, the Ag NPs in this composite are stable in air.

3.2. *Effect of the content of Ag NPs on the catalytic activity of the SG/RGO/Ag composite*

Currently, organic dyes in textiles, paper and plastic are one of the main sources of water pollution due to their toxicity and resistance to aerobic degradation. With RhB as a model

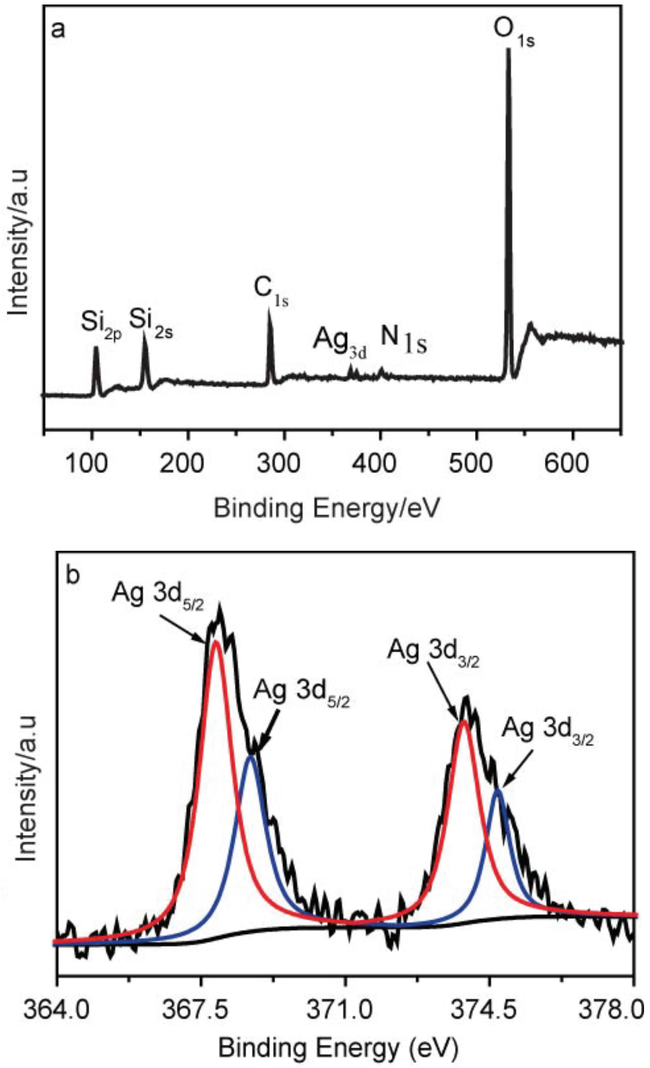

Fig. 2. XPS survey spectrum of the SG/RGO/Ag composite (a) and high-resolution XPS spectrum of the Ag3d (b).

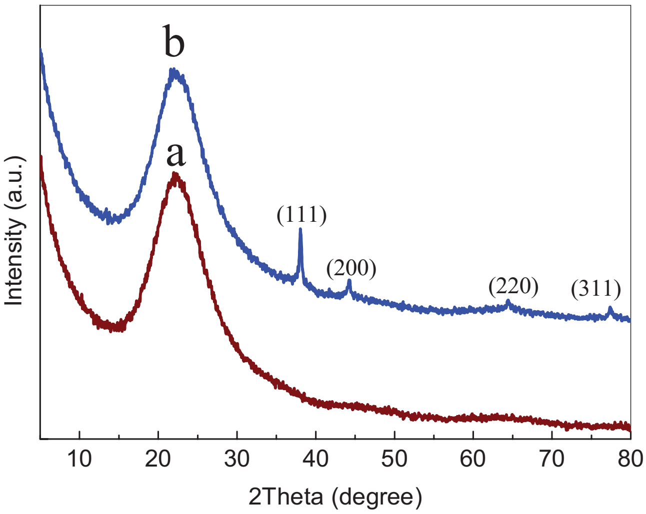

Fig. 3. XRD patterns of the SG/RGO (a) and SG/RGO/Ag (b).

pollutant, the catalytic activity for the degradation of RhB is carried out, and the influence of various factors on the catalytic activity of the SG/RGO/Ag composite is investigated.

In the composite, Ag NPs are the main active sites for the degradation of RhB. The relationship between loading amount of Ag NPs and the catalytic activity of the SG/RGO/Ag composite was investigated first. In our experiment, the SG/RGO/Ag with 0.78% Ag NPs was prepared first, and then its catalytic activity was investigated. It was found that it showed higher catalytic activity (Fig. 4). According to the optimal value of 0.78%, we choose a few points around it. Moreover, the addition of silver ions was almost loaded on the surface of GO and reduced by the sodium borohydride (It can be proved from no scattered Ag NPs outside of the SG (Figs. 1(c) and (d)), and no surface plasmon resonance peak of Ag in UV–visible spectrum of the solution (not shown here)). That is, the theory loading amount of Ag NPs is almost equal to the actual loading amount of Ag NPs. As shown in Fig. 4, when the content of Ag NPs is 0.78%, the degradation activity for RhB reaches the maximum. When the content of Ag NPs is lower than 0.78%, the degradation efficiency of RhB increases significantly with the increment of Ag NPs. The result suggests that increasing the content of Ag NPs is beneficial to enhance the degradation efficiency of RhB. However, when the loading amount of Ag NPs is beyond 0.78%, the degradation activity for RhB is gradually decreased. The possible explanation is that higher loading of Ag NPs could lead to the aggregation of Ag NPs. Hence, the contact area between RhB and the SG/RGO/Ag composite is reduced, which is bad for degradation of RhB [20]. According to the result in Fig. 3, the optimal loading amount of Ag NPs in the composite is 0.78%.

3.3. Effect of $NaBH_4$ dosage on the catalytic activity of the SG/RGO/Ag composite

In the degradation process of RhB, BH_4^- acted as the electron donor. The effect of $NaBH_4$ dosage on the catalytic

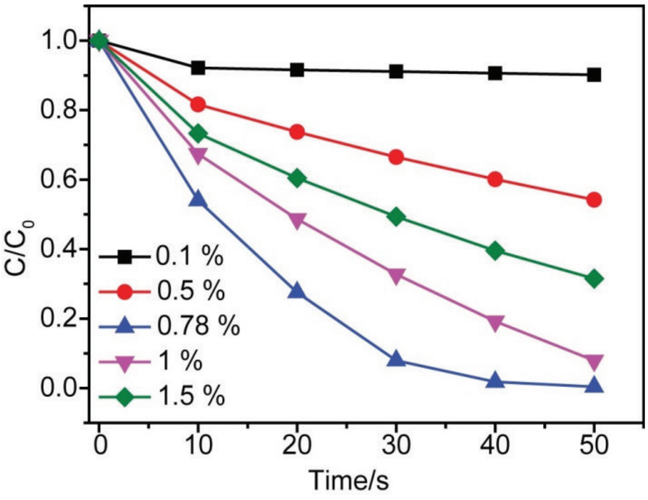

Fig. 4. Effect of loading amount of Ag NPs on the catalytic activity of the SG/RGO/Ag. Reaction conditions: initial concentration of RhB: 5 mg L^{-1}; temperature: 25°C; the amount of the catalyst: 0.4 g L^{-1}; volume ratio of $NaBH_4$ to RhB: 8:100; pH: 6.3; C_0 and C are the concentration after adsorption/desorption equilibrium and the concentration at a certain time, respectively.

activity of the SG/RGO/Ag is studied. As illustrated in Fig. 5, the degradation efficiency of RhB increases gradually with increasing the $NaBH_4$ dosage. However, in the absence of SG/RGO/Ag composite, the degradation is hardly observed. It can be explained by the following two reasons: first, in the initial stage of the catalytic reaction, Ag NPs are surrounded by RhB molecules, which make the Ag NPs be with relatively high Fermi level. After the addition of the $NaBH_4$, BH_4^- ions will adsorb onto the surface of Ag NPs through competitive adsorption. It could provide more electrons for Ag NPs [21]. Consequently, the potential difference could drive the RhB molecules to be degraded. Second, $NaBH_4$ could also promote the dissociation of RhB molecules, which is also beneficial to improve the degradation efficiency of RhB to a certain extent.

3.4. Effect of pH value on the catalytic activity of the SG/RGO/Ag composite

The pH value of the solution is usually an important factor affecting degradation of organic pollutants. With the SG/RGO/Ag as the catalyst, the influence of pH value on the degradation of RhB is explored. As can be seen from Fig. 6, the degradation efficiency of RhB has a close relationship with the pH value. The SG/RGO/Ag composite exhibits higher degradation efficiency for RhB under the neutral condition. The degradation efficiency is highest when the pH is 6.3. It is known that the pH value will affect the formation of RhB, and also affect the charge on the surface of the catalyst [22,23]. There exist two kinds of RhB in different pH solution, cationic (RhB^+) and zwitterionic ($RhB^\pm$) forms [24]. The reducibility of $NaBH_4$ will be reduced in acidic environment. When pH value is higher than pK_a of RhB (3.7), RhB ions are in the form of $RhB^\pm$, which is favorable to the adsorption and degradation of RhB molecules. However, RhB molecules in the form of $RhB^\pm$ are easily aggregated in alkaline condition through electrostatic interaction, which would inhibit the degradation of RhB. Subsequently, the interaction among catalyst, $NaBH_4$ and RhB is hindered under acidic or alkaline condition.

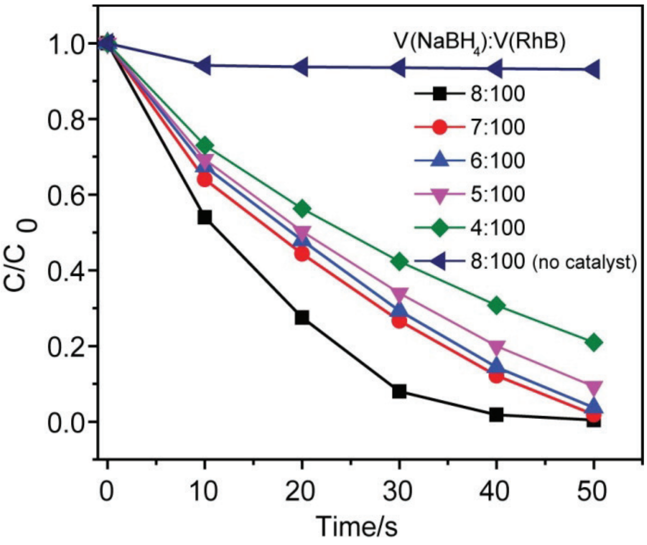

Fig. 5. Effect of $NaBH_4$ dosage on the degradation of RhB. Reaction conditions: loading amount of Ag NPs: 0.78%; initial concentration of RhB: 10 mg L^{-1}; temperature: 25°C; dosage of the catalyst: 0.4 g L^{-1}; pH: 6.3.

3.5. Effect of the amount of the catalyst on the catalytic activity of the SG/RGO/Ag composite

The amount of the catalyst is an important parameter affecting the degradation efficiency of organic pollutants. Fig. 7 shows the kinetic curves of the SG/RGO/Ag composite for degradation of RhB as a function of the amount of the catalyst. The result shows that the degradation efficiency is improved followed by increasing the amount of catalyst. This is mainly attributed to the

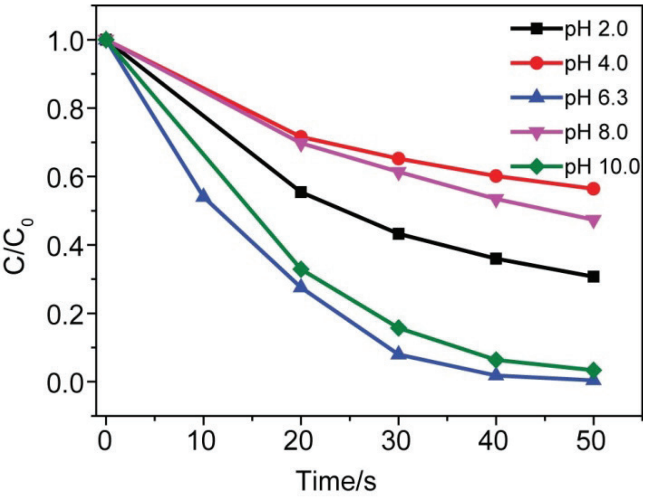

Fig. 6. Effect of pH value on the degradation of RhB. Reaction conditions: loading amount of Ag NPs: 0.78%; initial concentration of RhB: 5 mg L^{-1}; temperature: 25°C; ratio of V($NaBH_4$) to V(RhB): 8:100; amount of the catalyst: 0.4 g L^{-1}.

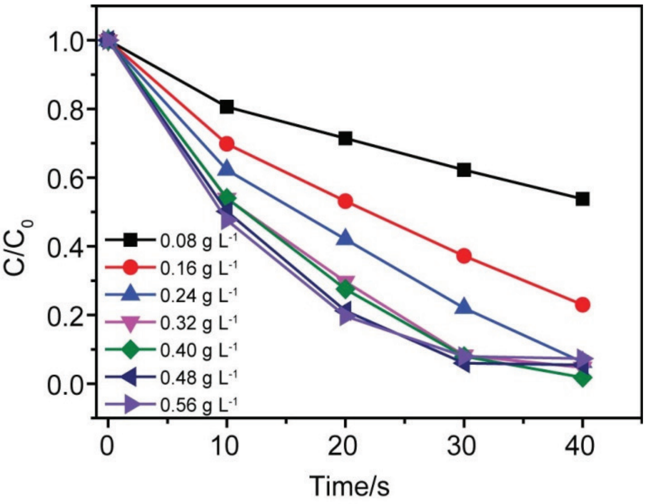

Fig. 7. Effect of the amount of the catalyst on the degradation of RhB. Reaction conditions: loading amount of Ag NPs: 0.78%; initial concentration of RhB: 5 mg L^{-1}; temperature: 25°C; ratio of V($NaBH_4$) to V(RhB): 8:100; pH: 6.3.

increased active sites that could accelerate the production of reactive oxygen species on the surface of the catalyst [25]. When the amount of the catalyst is beyond 0.4 g L^{-1}, some active sites may be covered by each other, so that the degradation efficiency of the RhB could not be improved obviously [26].

3.6. Effect of the concentration of RhB on the catalytic activity of the SG/RGO/Ag composite

The initial concentration of the dyes in the wastewater has a significant effect on the catalytic degradation efficiency. Fig. 8 shows the influence of the concentration of RhB on the degradation efficiency. It can be seen that the degradation efficiency of RhB is quickly enhanced when the concentration of RhB is less than 10 mg L^{-1}, and it is degraded completely within 50 s. The reason is that the degradation rate of RhB is dependent on the concentration of hydroxyl radicals produced [26]. When the concentration of RhB is increased, there exists a higher probability for the collision among RhB molecules and active sites on the surface of the catalyst, which increases the degradation efficiency [25,27]. However, when the concentration of RhB is higher than 10 mg L^{-1}, some small molecules produced in the degradation process of the RhB could occupy the active sites of the catalyst, and decrease the degradation rate [28]. It is known that the organic pollutants with low concentration are difficult to be removed by coagulation, filtration and adsorption. The SG/RGO/Ag composite shows its superiority in quick degradation for RhB with lower concentration, which is very important to the efficient treatment of pollutants in wastewater.

3.7. Effect of inorganic salts on the catalytic activity of the SG/RGO/Ag composite

In industrial production, inorganic salts are often added to improve the dyeing rate of dye, which results in the wastewater containing inorganic salts. Using the SG/RGO/Ag composite as the catalyst, the effect of some inorganic salts on the degradation of RhB is investigated.

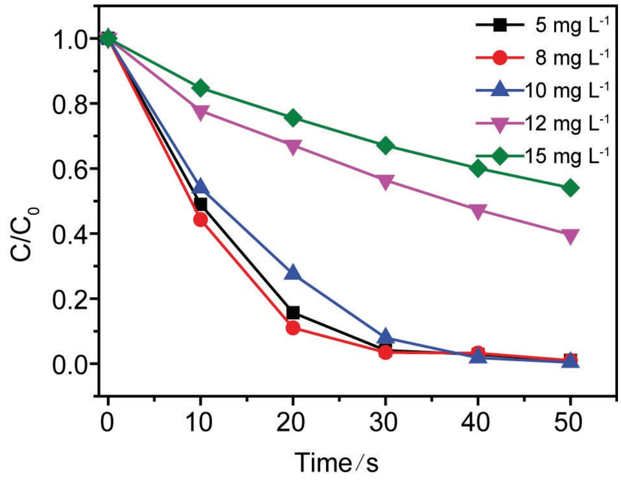

Fig. 8. Effect of the concentration of RhB on the degradation of RhB. Reaction conditions: loading amount of Ag NPs: 0.78%; temperature: 25°C; ratio of V($NaBH_4$) to V(RhB): 8:100; amount of the catalyst: 0.4 g L^{-1}; pH: 6.3.

As shown in Fig. 9 and Table 1, the introduction of SO_4^{2-} and NO_3^- improves the degradation rate of RhB. It is also found that Cl^- significantly inhibits the degradation of RhB. It may be attributed to the competitive adsorption of Cl^- and RhB on the surface of the SG/RGO/Ag [29], and also Cl^- consumes more ·OH. In addition, the degradation of RhB is inhibited in the presence of Mg^{2+}, Ca^{2+}, Na^+ and K^+. Moreover, the inhibitory effect of Mg^{2+} and Ca^{2+} is relatively obvious than that of Na^+ and K^+. It is probably due to the higher stability of their hydrated ions [25]. Subsequently, the introduction of Mg^{2+} or Ca^{2+} could cause the concentration of RhB be relatively higher in solution, and the degradation efficiency is decreased. It is consistent with the result shown in Fig. 7. Based on the above results, inorganic salts and dyes in the wastewater will competitively adsorb on the surface of the catalyst or directly react with the reactive oxygen species, and have an important influence on the degradation of dyes. Therefore, it is necessary to consider the influence of inorganic salts on the degradation of dyes in wastewater.

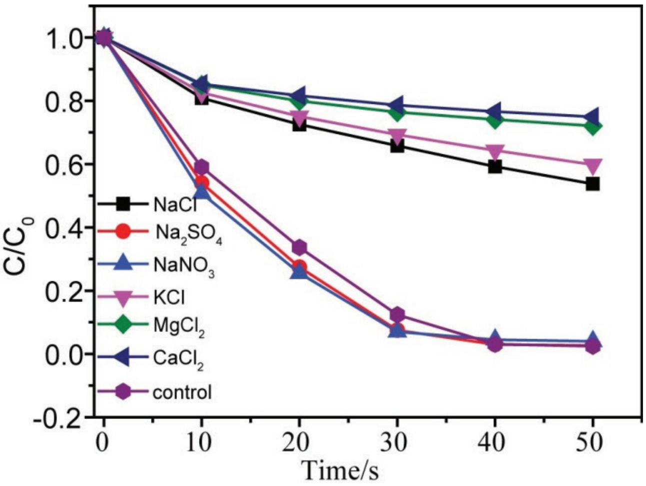

Fig. 9. Effect of inorganic salts on the degradation of RhB. Reaction conditions: loading amount of Ag NPs: 0.78%; temperature: 25°C; ratio of V($NaBH_4$) to V(RhB): 8:100; amount of the catalyst: 0.4 g L^{-1}; pH: 6.3; the concentration of salts: 0.1 mol L^{-1}; ratio of V(salt) to V(RhB): 1:25.

Table 1
The degradation efficiency (reacted for 30 s) of RhB in the presence of inorganic salts

Ion species	Degradation efficiency of RhB (%)
Ca^{2+}	21.4
Mg^{2+}	23.6
K^+	30.7
Na^+	34.2
Without adding salts	87.8
Cl^-	34.2
SO_4^{2-}	92.5
NO_3^-	92.9

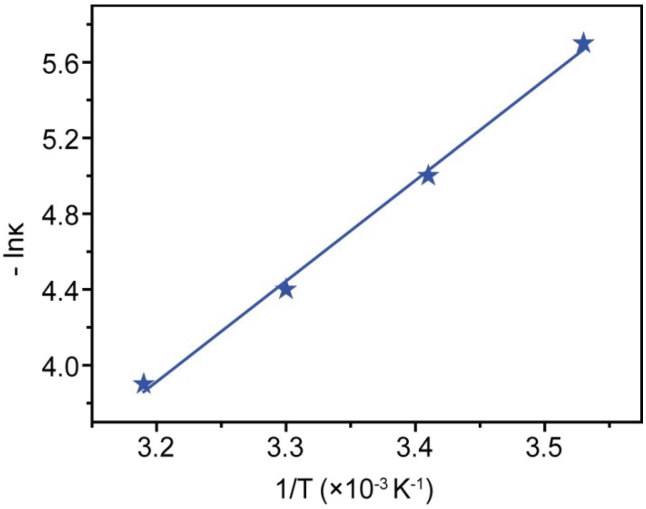

Fig. 10. Effect of temperature on the catalytic activity of the SG/RGO/Ag. Reaction conditions: loading amount of Ag NPs: 0.78%; initial concentration of RhB: 5 mg L^{-1}; amount of the catalyst: 0.08 g L^{-1}; ratio of V($NaBH_4$) to V(RhB): 8:100; pH: 6.3 (where the slope of the plotting of –ln(C/C_0) vs. reaction time is the apparent rate constant κ).

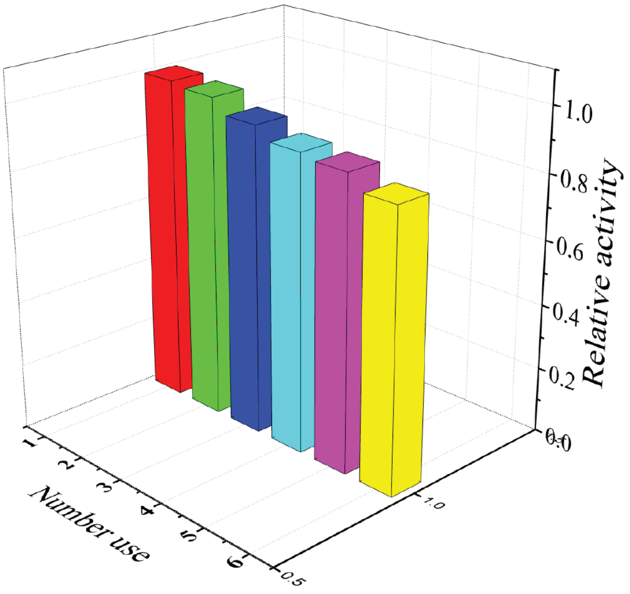

Fig. 11. Reusability of the SG/RGO/Ag nanocomposite for the catalytic degradation of RhB. loading amount of Ag NPs: 0.78%; initial concentration of RhB: 5 mg L^{-1}; amount of the catalyst: 0.4 g L^{-1}; ratio of V($NaBH_4$) to V(RhB): 8:100; pH: 6.3; temperature: 25°C.

3.8. The effect of temperature on the catalytic activity of the SG/RGO/Ag composite

The kinetic curves of RhB degradation at 10°C, 20°C, 30°C and 40°C are shown in Fig. 10. The degradation rate improves with the increment of the temperature. It is mainly due to the increment of reaction rate of $NaBH_4$ and the catalyst at higher temperature, which is profitable to the generation of ·OH, and then quickens the degradation of RhB. The reaction activation energy (E_a) of the SG/RGO/Ag composite is calculated to be 44.06 kJ mol^{-1} according to the plotting of lnκ against 1/T (Fig. 10) and the Arrhenius equation. The value is much higher than that reported in the literature [30,31]. Obviously, improving temperature has a positive influence on the degradation of RhB with the SG/RGO/Ag composite as the catalyst. In order to operate conveniently and save energy, in this manuscript, the degradation of RhB is carried out at about 25°C.

3.9. Stability and reusability of the catalyst

It is well known that the stability and reusability of a catalyst is important in practical application. Thus, the recyclability of the SG/RGO/Ag for the degradation of RhB was studied. After each run, the solid was carefully separated from the mixture by centrifugation, and then the dried solid was used as the catalyst in next run. The above process was repeated for six cycles. The results are shown in Fig. 11. Clearly, after six cycles, the degradation efficiency of RhB with the SG/RGO/Ag as the catalyst could still reach about 85%, suggesting that the SG/RGO/Ag composite possesses high catalytic activity and stability for the degradation of RhB.

4. Conclusions

The SG/RGO/Ag composite was achieved by electrostatic interaction combined with one-step reduction. As a catalyst, the composite showed a higher catalytic activity for the degradation of RhB, and RhB was degraded quickly (about 40 s) in an optimum condition. It was also shown that the optimal loading amount of Ag NPs was only 0.78%, and the degradation efficiency of RhB was improved after increasing the amount of $NaBH_4$ and the reaction temperature. Moreover, the SG/RGO/Ag composite was of low cost, high catalytic stability and facile recovery. The composite could be a potential candidate for degradation of organic dyes in wastewater treatment.

Acknowledgments

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