



Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature

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ABSTRACT

Persulfate (PS) oxidative degradation of azo dye acid orange 7 (AO7) in an aqueous solution was studied in the presence of suspended granular activated carbon (GAC) at ambient temperature (e.g., 25 °C). It was observed that there existed a remarkable synergistic effect in the GAC/PS combined system. Higher PS concentration and GAC dosage resulted in higher AO7 degrading rates. Near-neutral was the optimal initial pH. Adsorption had an adverse effect on AO7 degradation. AO7 had not only a good decolorization, but a good mineralization. The decomposition of PS followed a first-order kinetics behavior both in the presence and in the absence of AO7. Radical mechanism was studied and three radical scavengers (methanol (MA), *tert*-butanol (TBA), phenol) were used to determine the kind of major active species taking part in the degradation of AO7 and the location of degradation reaction. It was assumed that the degradation of AO7 did not occur in the liquid phase, but in the porous bulk and boundary layer on the external surface of GAC. $\text{SO}_4^{\cdot-}$ or HO^{\cdot} , generated on or near the surface of GAC, played a major role in the AO7 degradation. Finally, the recovery performance of GAC was studied through the GAC reuse experiments.

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1. Introduction

Textile industries produce a great deal of wastewater polluted with dyes [1]. There are about 1,000,000 tons of different dyes produced annually in the world [1]. Azo dyes constitute the largest and the most important class of commercial dyes, accounting for 50% of all commercial dyes [2]. They are characterized by nitrogen-to-nitrogen double bonds (N=N). The release of these compounds into water streams is undesirable, not only because of their color, but also because many azo dyes have caused several ecological and environmental problems owing to their toxic, non-biodegradation and potentially carcinogenic [1,3]. They are abated by some non-destructive process, such as activated carbon adsorption and membrane filtration, in which the degradation and mineralization of dyes could not be achieved [4]. Therefore, the development of destructive process for dyeing wastewater degradation has aroused significant interest currently [4].

Advanced oxidation processes (AOPs) have been developed to degrade biorefractory organics in drinking water and indus-

trial effluents [5]. Activated persulfate (PS) oxidation is a recently emerging AOP for organic pollutant degradation [6]. PS has an O–O bond, whose energy is 140 kJ/mol [7]. PS presents limited ability to oxidize organics independently [8–10]. However, under activation conditions of heating [8,10–13], UV-light [14–16] or transition metal ions [9,13,17–19], PS can generate free radicals $\text{SO}_4^{\cdot-}$, with oxidation–reduction potential of +2.5 to +3.1 V vs. NHE (normal hydrogen electrode) [20], which can oxidize most of the organics in water [21].

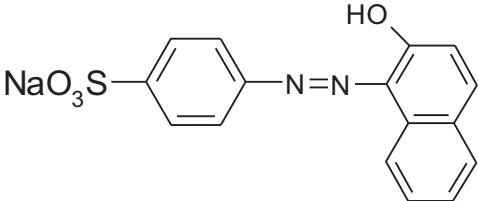
Granular activated carbon (GAC) is widely used as an adsorbent in purification of gases and liquids. GAC is not only an adsorption material, but also a catalyst carrier and a catalyst [22]. As a catalyst, GAC is in conjunction with a variety of oxidants, such as H_2O_2 [23–34] and O_3 [35]. There are lots of studies about using the combined systems of GAC and H_2O_2 (GAC/ H_2O_2 [23–26], GAC/ H_2O_2 /UV light [27,28], GAC/Fenton [29–32], GAC/wet H_2O_2 oxidation [33,34]) to degrade the organics in water or wastewater, which is based on the fact that H_2O_2 can interact with GAC surface and then produce radicals (HO^{\cdot} or HO_2^{\cdot}) with stronger oxidation ability [36]. GAC acts in a way which is similar to iron(II) ion in the Fenton's reagent and acts as a catalyst of the electron-transfer mediator [23].

As is well known, persulfate (PS) is similar in structure to H_2O_2 . So PS may be catalyzed by GAC too, involving the formation of free radicals of sulfate radical ($\text{SO}_4^{\cdot-}$) [37]. The predicted reaction

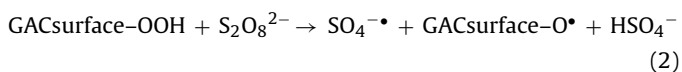
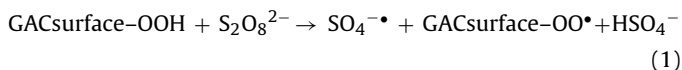
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Table 1
Characteristics of acid orange 7.

Chemical structures	Molecular weight (g mol ⁻¹)	λ_{\max} (nm)	Molecular formula
	350.33	484	C ₁₆ H ₁₁ N ₂ NaO ₄ S

mechanisms are assumed as follows [37]:



However, few studies have investigated the presence of active species and the reaction area of the active species with organic substances, and the mechanism of organic degradation by GAC/PS is not clear yet.

Azo dye acid orange 7 (AO7) has commonly been used as a model compound for the degradation of dyes [1,2,5,38–42]. The degradation of the model organic contaminant AO7 in aqueous solution by GAC catalyzed PS oxidation has been studied detailedly in this paper. The study seeks to answer the following questions in the GAC/PS combined system. (1) Does there exist a synergistic effect? How do the four operational parameters (PS concentration, GAC dosage, initial pH and the adsorbent on GAC) affect the AO7 degradation? Can the organic contaminant be mineralized? (2) Whether PS could be decomposed catalyzed by GAC? (3) Which kind of active species mainly take part in the degradation process and what is the possible reaction area of active species with organic substances? (4) Could GAC be reused for several times?

2. Experimental

2.1. Material

Sodium persulfate (PS, Na₂S₂O₈), acid orange 7 (AO7, 4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid), methanol (MA, CH₃OH), *tert*-butyl alcohol (TBA, C₄H₉OH), sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), sodium bicarbonate (NaHCO₃), phenol (C₆H₆O), and potassium iodide (KI) were purchased from Shanghai Chemical Reagent Company, China, reagent-grade and used without purification. The molecular structure of AO7 was shown in Table 1. All experiments were carried out using double distilled water. Commercial granular active carbon (GAC, Shanxi Xinhua Chemical Factory, China), with a diameter of 1.5 mm, a height of 4.0 mm and specific surface area of 900 m²/g, was washed with 10% dilute hydrochloric acid and distilled water in turn, and then dried at 105 °C for 24 h. The AO7 spent-GAC was prepared as follows: GAC (1.0 g) was added into 250 mL AO7 (20 mg/L) aqueous solution and the suspension was stirred for 3–4 days until the concentration of AO7 in the suspension no longer changed. The GAC, filtered from the suspension, dried at 105 °C for 24 h, was marked as the AO7 spent-GAC.

2.2. Reactor and procedure

The general degradation reactions were carried out in 500 mL conical flasks. The temperature of the reacting solution was

kept constant throughout the experiments. All experiments were performed under the atmospheric pressure and at ambient temperature (e.g., 25 °C).

In the experiments of GAC catalyzed PS oxidation, the AO7 solution (250 mL) and oxidant (PS) was added into the reactor before the reaction. The initial concentration of AO7 was all kept at 20 mg/L. The initial pH of the solution was not adjusted and was 5.1 under the condition of PS/AO7 molar ratio 100/1. Then a certain amount of GAC was added into the reactor which contained AO7 and PS, and the reactor was placed in a rocker, whose swing speed was 300 rpm. The reaction time of each experiment was exactly 5 h. At given intervals of reaction, 4 mL of the supernatant was quickly sampled and filtered for analysis.

In the experiments of the effect of initial pH on the degradation, the initial pH was adjusted by 0.1 M NaOH or 0.1 M H₂SO₄ before adding GAC to the solution. Other operating steps were the same as the experiments of GAC catalyzed PS oxidation. In the experiments of the effect of the adsorbent on GAC on the degradation, the only difference is that the AO7 spent-GAC, instead of the normal GAC, was added into the solution.

2.3. Analysis

The UV–vis absorbance of the samples was analyzed with a Shimadzu UV1206 Spectrophotometer. The degradation of AO7 was monitored by measuring the maximum absorbance at $\lambda = 484$ nm as a function of irradiation time. Shimadzu TOC-VCPN was used to analyze total organic carbon (TOC) of the samples. The concentration of PS was determined by a UV spectrophotometric method [43].

Every experiment was carried out three times and the obtained results were similar, with variance not greater than 5%. The data referred to in this paper is the mean value.

3. Results and discussion

3.1. AO7 degradation by GAC catalyzed PS oxidation

In this study, both the adsorption of GAC and the oxidation of PS catalyzed by GAC induced AO7 removal in the GAC/PS system. Fig. 1 presents the degradation of AO7 by persulfate (PS) in the presence of GAC. Results show that, compared with the only PS oxidation system or the only GAC adsorption system, the GAC/PS combined system can induce AO7 degradation more significantly. The degradation of AO7 in the three systems (the only PS system, the only GAC system and the GAC/PS combined system) followed a first-order kinetics behavior ($R^2 > 0.95$) and the rate constants were 0.010 h⁻¹, 0.042 h⁻¹ and 0.397 h⁻¹, respectively. It was presented in the inserted figure in Fig. 1. Therefore, it was obvious that there existed a remarkable synergistic effect in the GAC/PS combined system. These results were similar to other studies investigating the GAC/H₂O₂ combined system [23–26].

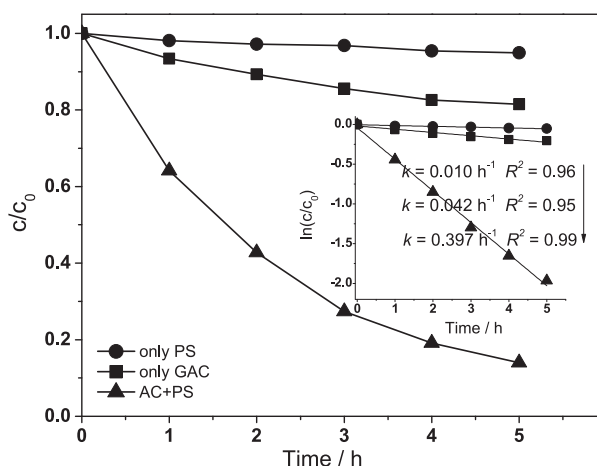


Fig. 1. Degradation of AO7 by the GAC/PS combined system. PS/AO7 molar ratio = 100/1, GAC dosage = 1.0 g/L.

In this part, the effects of PS concentration, GAC dosage, initial pH of the solution and the adsorbate on GAC on AO7 degradation by the GAC/PS combined system were discussed.

3.1.1. Effect of PS concentration

Fig. 2 illustrates that the raising of PS concentration can accelerate the AO7 degradation. The AO7 degradation rate was the highest when PS/AO7 molar ratio was 500/1. In comparison with the AO7 degradation at PS/AO7 molar ratio 50/1, there was a remarkable accelerating effect when PS/AO7 molar ratio increased to 100/1. However, further increase in the initial PS resulted in saturation. The degradation efficiencies of AO7 for every increase PS/AO7 molar ratio from 100/1 to 500/1 increased a little. Hori et al. [44] and Chu et al. [45] also had the same results that when the PS concentration increased beyond a numeric value, the increment of organics degradation rate slowed down slightly. It was reported that $\text{SO}_4^{\cdot-}$, produced by catalysis of PS, reacted with superfluous PS to form SO_4^{2-} [46].

3.1.2. Effect of GAC dosage

Fig. 3 shows the effect of GAC dosage on the AO7 degradation by GAC catalyzed PS oxidation. With an increase of GAC, a faster AO7 degradation was observed both in the GAC adsorption system

and the GAC/PS combined system. It was because that wider GAC surface area increased the amount of active sites for adsorption and the activation of PS. There also existed a synergistic effect at 5.0 g/L GAC dosage, however, the effect was not as remarkable as that at 1.0 g/L GAC dosage. Considering the contribution made by GAC to the GAC/PS combined system, 1.0 g/L was the most efficient dosage in the GAC/PS combined system at PS/AO7 molar ratio 100/1.

3.1.3. Effect of initial pH

The influence of initial pH was also studied at GAC dosage 1.0 g/L, PS/AO7 molar ratio 100/1. As shown in Fig. 4, the fastest removal rate of AO7 in single GAC adsorption system occurred at initial pH 3.0, but that occurred at initial pH 5.1 in the GAC/PS combined system. The adsorption capacity of GAC increased with the decrease of the aqueous phase pH. GAC developed a positive surface charge when $\text{pH}(\text{solution}) < \text{pH}_{\text{PZC}}$ (potential of zero charge), and a negative charge when $\text{pH}(\text{solution}) > \text{pH}_{\text{PZC}}$ [47]. The pH_{PZC} of GAC in our studies was about 2.7 and AO7 was an anionic dye, so with the increase of the pH of aqueous phase, negative charge at GAC surface became stronger. Correspondingly, GAC surface repelled anionic dye AO7. The results of organic degradation altered in the presence of PS. The following order in the degradation of AO7 in the GAC/PS combined system at different initial pH was observed: (initial pH 5.1) > (initial pH 3.0) > (initial pH 11.0). GAC adsorbed more organics on its surface in a relatively acidic medium, which had an adverse effect on organic degradation in the GAC/PS combined system. It is because that oxidant itself does not effectively diffuse into pores filled with liquid organics [25]. However, when there was little adsorbent on GAC surface in an alkaline environment, the ratio of dye degradation was lower too. It may be because of the short lifetime of the free radicals (e.g., the lifetime of $\text{SO}_4^{\cdot-}$ and HO^{\cdot} are 4 s [48] and 20 ns [25], respectively). The free radicals cannot diffuse into the bulk phase to react with a substrate. Therefore, the pH of aqueous played a significant role on organic degradation in the GAC/PS combined system and near-neutral was the optimal initial pH for the AO7 degradation in the GAC/PS combined system.

3.1.4. Effect of adsorbate on GAC

As mentioned above, when GAC adsorbed more organics on its surface, there was an adverse effect on organic degradation in the GAC/PS combined system. In order to prove it, we have a hypothesis that AO7 should have much worse degradation efficiency in the AO7 spent-GAC/PS process than in the normal GAC/PS system. So, in this

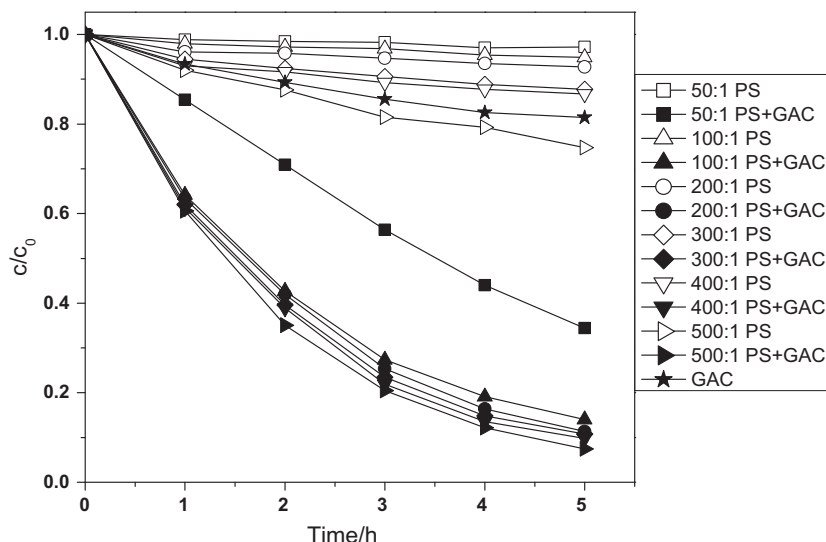


Fig. 2. Effect of PS concentration on the degradation of AO7 by the GAC/PS combined system. GAC dosage = 1.0 g/L, PS/AO7 molar ratio = 50/1–500/1.

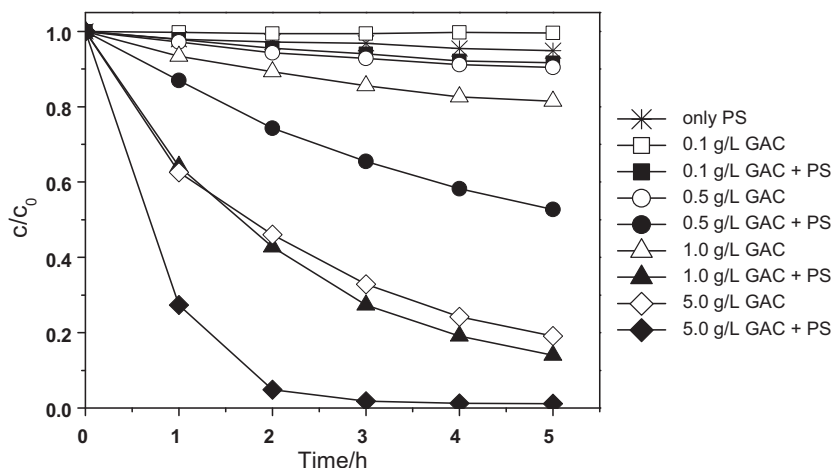


Fig. 3. Effect of GAC dosage on the degradation of AO7 by the GAC/PS combined system. PS/AO7 molar ratio = 100/1.

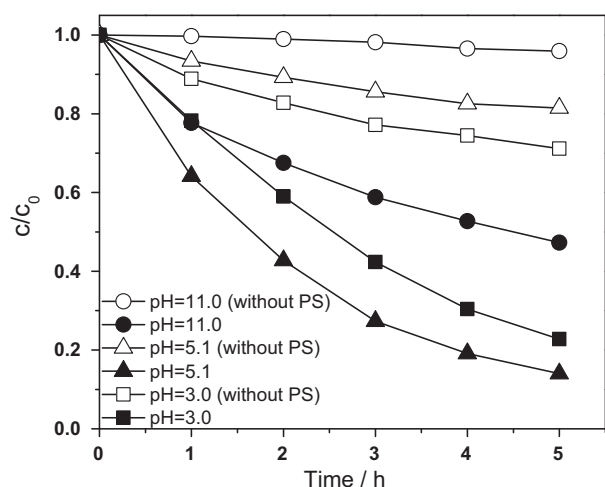


Fig. 4. Effect of initial pH on the degradation of AO7 by the GAC/PS combined system. GAC dosage = 1.0 g/L, PS/AO7 molar ratio = 100/1.

part, AO7 degradation by the AO7 spent-GAC, instead of the normal GAC, catalyzed PS oxidation was examined and other conditions were not changed (Fig. 5). It indicated that two kinds of GAC had a great difference in the adsorption process. And the degradation rate

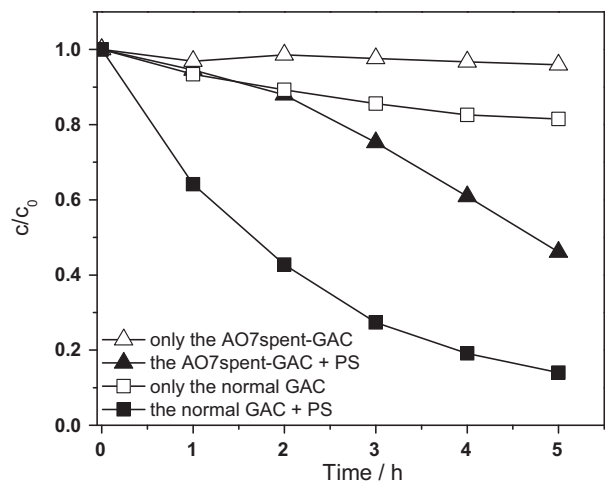


Fig. 5. Degradation of AO7 by the AO7 spent-GAC/PS combined system. PS/AO7 molar ratio = 100/1, GAC dosage = 1.0 g/L.

was much slower in the AO7 spent-GAC catalyzed system, which was coincident with our hypothesis. The loading dye molecules on the GAC surface decreased the active surface sites available for the activation of PS, which inhibited the degradation of AO7.

3.1.5. UV-vis spectra and the TOC removal

Fig. 6(a) illustrates the UV-vis spectra of the samples drawn at 0, 2.5 and 5 h at PS/AO7 molar ratio 100/1, GAC dosage 1.0 g/L, and initial pH 5.1. The UV-vis spectrum of the only PS without AO7 in the distilled water is also shown. Absorption spectrum of AO7 in water was mainly characterized by four bands. Two bands were seen at 484 nm and at 430 nm because of the hydrazone form and azo form of AO7 [49]. The other two bands in the ultraviolet region located at 230 nm and 310 nm were attributed to the benzene and naphthalene rings of AO7, respectively [50]. It was apparent in Fig. 6(a) that the intensity of characteristic band at 484 nm and 310 nm were found to diminish during the experiment and the removal efficiencies of these bands were above 80% and 50% in 5 h reaction, respectively. It was speculated that AO7 must have been partly mineralized by PS in the presence of GAC. In order to demonstrate this speculation, the TOC removal experiment was conducted as follows, since it is a good indicator for mineralization of organics.

As stated in Fig. 6(b), TOC decreased rapidly to 37% removal in the first 2.5 h reaction and 11% reduction was observed in the latter 2.5 h. There was a similar reduction trend in UV-vis spectra. The degradation of AO7 was rapid in the first 2.5 h reaction and slower in the latter 2.5 h. It can be deduced that the reaction took place rapidly in the first stage after the beginning of the reaction, yet slowed down subsequently. The reason may be that: (1) intermediate compounds that were difficult to mineralize interfered with the reaction; (2) PS was difficultly decomposed by GAC when PS concentration became lower in the latter 2.5 h. Therefore, the PS decomposition catalyzed by GAC was also studied in the following section.

3.2. PS decomposition catalyzed by GAC

The effects of PS concentration and GAC dosage on the PS decomposition in the presence of AO7 are shown in Fig. 7(a) and (b). It can be seen that the decomposition of PS followed a first-order kinetics behavior. With an increase of GAC dosages, a faster PS decomposition was observed. When the PS concentration was increased, PS decomposition rate decreased. What is more, PS decomposition rate was still high in the latter 2.5 h, which was different from the reduction trend in UV-vis spectra and TOC of AO7 in Fig. 6. So the reason why AO7 degradation was slow in the latter 2.5 h should be

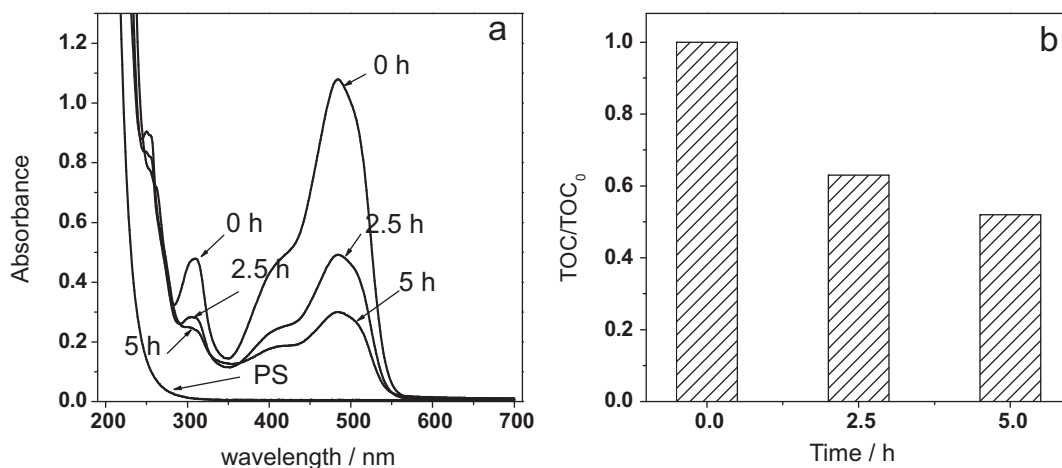


Fig. 6. UV-vis spectra (a) and TOC removal (b) of AO7 degradation by the GAC/PS combined system. PS/AO7 molar ratio = 100/1, GAC dosage = 1.0 g/L.

that intermediate compounds which were difficult to mineralize interfered with the reaction. As shown in Fig. 7(c), in the absence of AO7, the decomposition rate of PS catalyzed by GAC increased and still followed a first-order kinetics behavior. Similar results have been obtained in the GAC/H₂O₂ combined system [24,25]. The reduction in the decomposition rate has attributed to the loading of GAC with organic sorbates and the reduction in active surface sites available for the activation of PS.

3.3. Radical mechanism

As mentioned above (Eqs. (1) and (2)), PS may be catalyzed by GAC, involving the formation of free radicals of SO₄^{-•} [37]. The presence of SO₄^{-•} in aqueous solution can result in radical interconversion reactions to produce the hydroxyl radical (HO[•]), with oxidation–reduction potential of +1.8 V to +2.7 V vs. NHE [21] in accordance with the following reactions

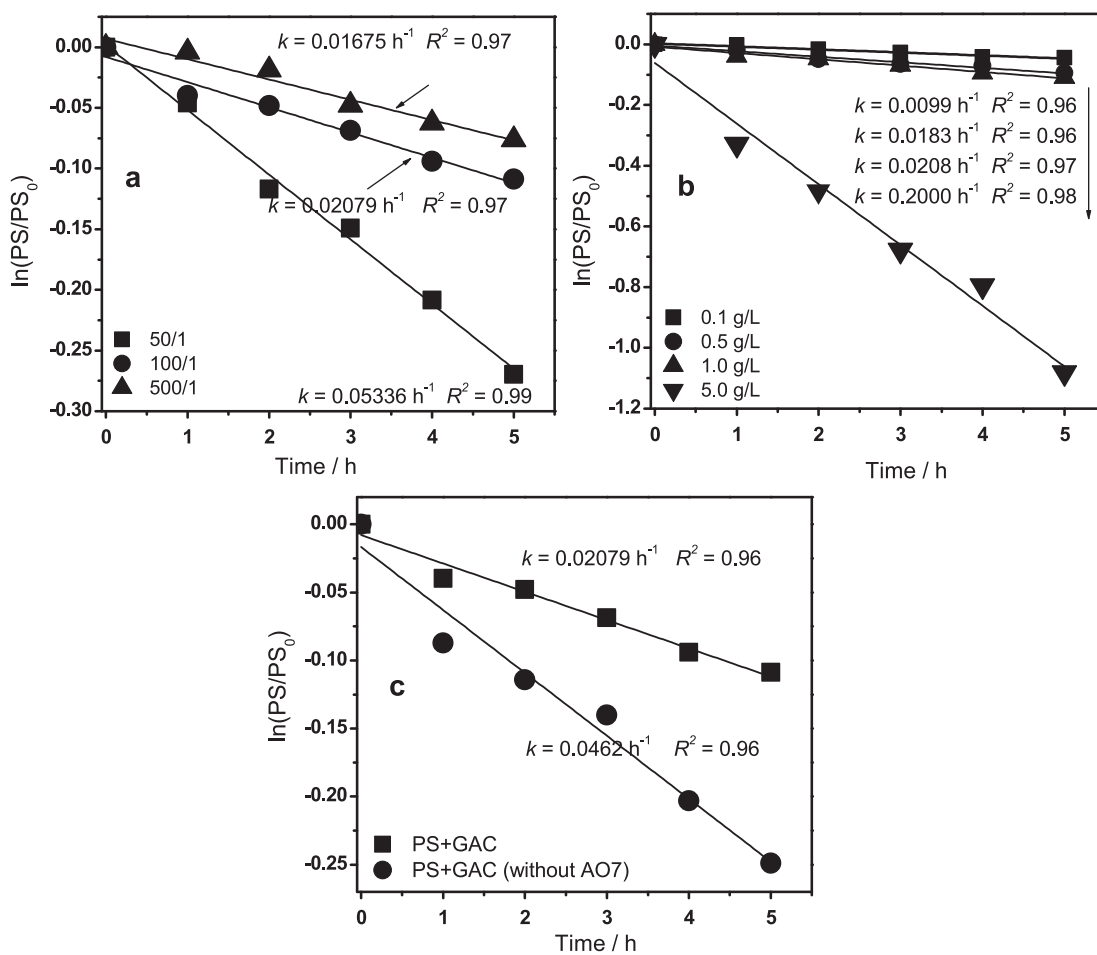


Fig. 7. Effect of PS concentration on PS decomposition at the fixed GAC dosage = 1.0 g/L (a), effect of GAC dosage on PS decomposition at the fixed PS/AO7 molar ratio = 100/1 (b), and effect of the absence of AO7 on PS decomposition at PS/AO7 molar ratio = 100/1, GAC dosage = 1.0 g/L (c) in the GAC/PS combined system.

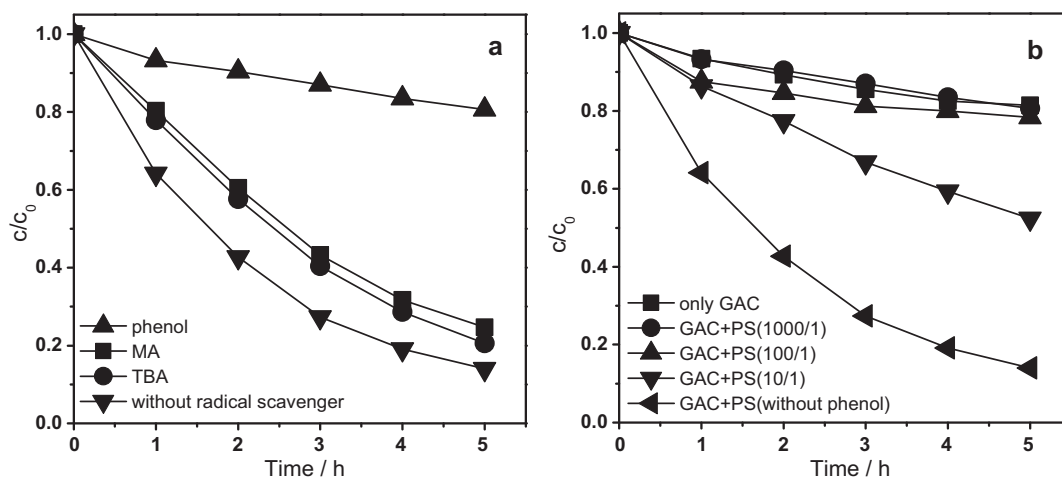
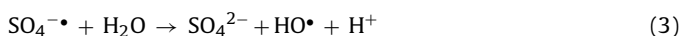


Fig. 8. Reaction of AO7 in the presence of different radicals scavengers at [radicals scavengers]/AO7 = 1000/1 (a), and different concentration of phenol at phenol/AO7 molar ratio = 10/1, 100/1, 1000/1 (b) in the GAC/PS combined system. PS/AO7 molar ratio = 100/1, GAC dosage = 1.0 g/L.

[10,51]:



Both $\text{SO}_4^{\cdot-}$ and HO^{\cdot} are possibly responsible for the destruction of organic contaminants in the GAC/PS combined system.

It is thoroughly established in the literature that alcohols containing alpha hydrogen can readily react with $\text{SO}_4^{\cdot-}$ and HO^{\cdot} [52], such as methanol (MA) ($k_{\text{SO}_4^{\cdot-}/\text{MA}} = 1.6 \times 10^7 - 7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{HO}^{\cdot}/\text{MA}} = 1.2 \times 10^9 - 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [20,21]. When Georgi et al. [25] added MA into the GAC/ H_2O_2 suspension, the reaction of the contaminants slowed down. It was because that there were free radicals HO^{\cdot} in the GAC/ H_2O_2 suspensions. *Tert*-butanol (TBA) is also an effective quenching agent for HO^{\cdot} , and it reacts much slower with $\text{SO}_4^{\cdot-}$; the reaction rate with HO^{\cdot} ($k_{\text{HO}^{\cdot}/\text{TBA}} = 3.8 \times 10^8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is approximately 1000-fold greater than that with $\text{SO}_4^{\cdot-}$ ($k_{\text{SO}_4^{\cdot-}/\text{TBA}} = 4 \times 10^5 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [20,21]. Some experiments were also carried out in ozonation of dimethyl phthalate (DMP) over catalyzed by Ce/GAC in the presence of TBA, and the degradation of DMP was strongly inhibited in the presence of TBA [53]. However, in our studies, when MA or TBA (alcohol/AO7 molar ratio 1000/1) was added into the GAC/PS suspensions, the inhibiting effects of AO7 degradation were not obvious, seen from Fig. 8(a).

However, phenol, another strong quencher of $\text{SO}_4^{\cdot-}$ and HO^{\cdot} radicals ($k_{\text{SO}_4^{\cdot-}/\text{phenol}} = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{HO}^{\cdot}/\text{phenol}} = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [54,55], exerts a strong inhibiting effect in the GAC/PS systems (as shown in Fig. 8(a)). When phenol was added into the GAC/PS suspensions containing AO7, the reaction of AO7 degradation slowed down and the inhibiting effect increased with the concentration of phenol added, as shown in Fig. 8(b). When phenol/AO7 molar ratio in the suspension was 1000/1, the oxidation of PS induced by GAC was almost stopped, and the two lines of oxidation and only adsorption nearly coincided.

Since MA and TBA are hydrophilic compounds, they cannot be assumed to accumulate on the GAC surface to a significant extent. They should rather be competitors for reactions with $\text{SO}_4^{\cdot-}$ and HO^{\cdot} radicals taking place in liquid phase. Phenol, often removed by GAC adsorption [56], is easier to approach carbon surface. Therefore, phenol could react with free radicals which exist in close proximity to GAC surface. Besides, oxygen surface function groups, such as carboxylic, phenolic, lactonic, which play a substantial role in catalytic oxidation of GAC, are on edge carbon atoms of aromatic rings of the sorbent graphic structure, so oxidant decomposes

without involving the carbon surface [57]. Therefore, in our experiments, the areas of reacting with the free radicals with AO7, most likely, were the porous bulk or the boundary layer on the external surface of GAC granules. Phenol would be a competitor for reactions with free radicals taking place in the porous bulk and boundary layer on the external surface of GAC. And, the active species which took part in the AO7 degradation by the GAC/PS combined system was $\text{SO}_4^{\cdot-}$ or HO^{\cdot} .

3.4. Reuse of GAC

The reuse experiment was carried out to detect the recovery performance of GAC. The results are shown in Fig. 9. The efficiencies of AO7 removal for every reuse cycle gradually decreased, but in the GAC/PS combined system, when GAC was used for the fourth time, the degradation ratio of AO7 was still over 60% in 5 h reaction. It implied that the GAC had slightly deactivated and had not a very bad in situ recovery performance. This could be due to the following reasons: (1) the incomplete removal of AO7 adsorbed on GAC surface inhibited the interaction of GAC and PS; (2) the intermediate products of AO7 decomposition remaining on the surface of GAC was not advantageous for the degradation reaction; (3) the adsorbed fraction of organic contaminants on the GAC surface was nearly unreactive. Liang et al. [37] also had the same

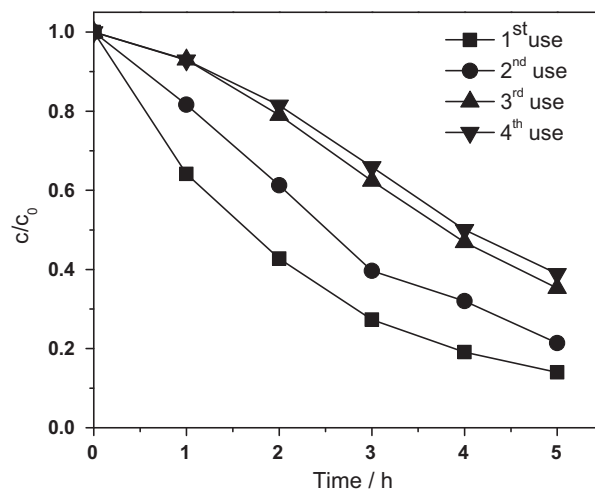


Fig. 9. GAC reuse in the GAC/PS combined system. PS/AO7 = 100/1, GAC dosage = 1.0 g/L.

results, when they used PS to regenerate the trichloroethylene spent-GAC.

4. Conclusions

In summary, GAC catalyzed PS oxidation at ambient temperature (e.g., 25 °C) had much better effect on the removal of AO7 than the process of only PS or GAC. It was observed that there existed a remarkable synergistic effect in the GAC/PS combined system. For the GAC/PS combined system, higher PS concentration and GAC dosage resulted in higher AO7 degradation rates. The pH of aqueous played a significant role in organic degradation and near-neutral was the optimal initial pH. The AO7 spent-GAC, instead of normal GAC, catalyzed PS oxidation experiments proved that organic molecules which adsorbed on the GAC surface had an adverse effect on degradation of AO7 in the GAC/PS combined system. Moreover, the GAC/PS combined system had not only a good decolorization, but also a good mineralization.

The PS decomposition catalyzed by GAC followed a first-order kinetics behavior. With an increase of GAC dosages, a faster PS decomposition was observed. When the PS concentration was increased, the PS decomposition rate decreased. The decomposition rate of PS catalyzed by GAC in the absence of AO7 increased but still followed a first-order kinetics behavior.

Three radical scavengers (MA, TBA, phenol) were used to determine the dominant active species generated in the GAC/PS system. It was observed that the course of AO7 degradation by the GAC/PS system possibly did not occur in the liquid phase, but the porous bulk or the boundary layer on the external surface of GAC granules. And, the active species which took part in the organic degradation by the GAC/PS combined system was $\text{SO}_4^{\cdot-}$ or HO^{\cdot} , generated near or at the surface of GAC.

GAC could be reused for several times in the GAC/PS combined system. The efficiencies of AO7 removal for every reuse cycle gradually decreased, but in the GAC/PS combined system, when GAC was used for the fourth time, the degradation ratio of AO7 was still over 60% in 5 h reaction.

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