



A novel advanced oxidation process to degrade organic pollutants in wastewater: Microwave-activated persulfate oxidation

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Received 21 November 2008; revised 18 December 2008; accepted 03 January 2009

Abstract

This article, for the first time, provides a novel advanced oxidation process based on sulfate radical ($\text{SO}_4^{\cdot-}$) to degrade organic pollutants in wastewater: microwave (MW)-activated persulfate oxidation (APO) with or without active carbon (AC). Azo dye acid Orange 7 (AO7) is used as a model compound to investigate the high reactivity of MW-APO. It is found that AO7 (up to 1000 mg/L) is completely decolorized within 5–7 min under an 800 W MW furnace assisted-APO. In the presence of chloride ion (up to 0.50 mol/L), the decolorization is still 100% completed, though delayed for about 1–2 min. Experiments are made to examine the enhancement by AC. It is exciting to find that the 100% decolorization of AO7 (500 mg/L) is achieved within 3 min by MW-APO using 1.0 g/L AC as catalyst, while the degradation efficiency maintains at 50% by MW energy without persulfate after about 5 min. Besides the destruction of visible light chromophore band of AO7 (484 nm), during MW-APO, two bands in the ultraviolet region (228 nm and 310 nm) are rapidly broken down. The removal of COD is about 83%–95% for 500 mg/L AO7. $\text{SO}_4^{\cdot-}$ is identified with quenching studies using specific alcohols. Both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ could degrade AO7, but $\text{SO}_4^{\cdot-}$ plays the dominant role. In a word, MW-APO AC is a new catalytic combustion technology for destruction of organic contamination even for high concentration.

Key words: microwave-activated persulfate oxidation; active carbon; sulfate radical; advanced oxidation technology

DOI: 10.1016/S1001-0742(08)62399-2

Introduction

Advanced oxidation processes (AOPs) have been developed to degrade biorefractory organics in drinking water and industrial effluents. Almost all AOPs are based on the generation of the reactive species, hydroxyl radicals ($\cdot\text{OH}$, E^0 varied between +1.8 and +2.7 V vs. NHE) (Buxton *et al.*, 1988), which degrade a broad range of organic pollutants quickly and non-selectively (Tabrizi and Mehrvar, 2004; Klavarioti *et al.*, 2008).

Activated persulfate oxidation is a recently emerging AOP for organic pollutants degradation (Yang *et al.*, 2008). It is the newest form of oxidant being currently used for *in-situ* chemical oxidation (ISCO) to transform ground-water or soil contaminants into less harmful chemical species (Huling and Pivetz, 2006). The thermal (Huang *et al.*, 2002; Liang *et al.*, 2003; Liang and Bruell, 2008), photochemical (Hori *et al.*, 2005) or metal ions (Liang *et al.*, 2004) activated decomposition of persulfate anion ($\text{S}_2\text{O}_8^{2-}$) produce a powerful oxidant known as the sulfate free radical ($\text{SO}_4^{\cdot-}$, E^0 varied between +2.5 and +3.1 V vs. NHE) (Neta *et al.*, 1988). The formation of $\text{SO}_4^{\cdot-}$ may initiate a series of radical propagation and termination chain

reactions where organic compounds can be transformed.

The use of the UV-persulfate or heated-persulfate oxidation is a standard method for the determination of total organic carbon (TOC), nitrogen and phosphorus in water and wastewater (MacKinnon, 1978; Raimbault *et al.*, 1999; Karthikeyan *et al.*, 2009). However, for wastewater treatment, only a few reports have discussed organic pollutants direct-degradation by thermal, photochemical or metal ions activated persulfate oxidation (Hori *et al.*, 2005; Huang *et al.*, 2007; Rastogi *et al.*, 2008; Huang and Huang, 2009; Li *et al.*, 2008). On the other hand, little attention has been paid to the organic wastewater containing high salinity (Piscopo *et al.*, 2001). In some wastewater, the concentration of chloride can even be higher than 0.5 mol/L. Hence, it would be of both academic and practical interest to look into this problem, the studies of the treatment of high saline wastewater are worthwhile.

Recently, microwave (MW)-assisted reactions are well established and have gained popularity as indicated by a large number of publications (Kappe, 2004). The applications of MW energy to enhance environmental waste treatment (Abramovitch *et al.*, 1999; Jones *et al.*, 2002; Xia *et al.*, 2003; Bo *et al.*, 2008) have also been growing, due to the molecular-level heating of MW, which leads to homogeneous and quick thermal reactions (Menendez *et*

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al., 2002). Compared with common heating mode, MW heating can decrease activation energy, reduce reaction time, increase the selectivity of reaction, improve the speed of reaction, and so on. Activated carbon (AC), as an excellent MW absorbing material, could absorb and convert MW energy into thermal energy. MW combined with AC, has also been utilized in wastewater treatment (Tai and Jou, 1999; Liu *et al.*, 2004; Bo *et al.*, 2006).

In this study, a novel AOP based on sulfate radical ($\text{SO}_4^{\cdot-}$) for the destruction of organic pollutants in wastewater, i.e., microwave (MW)-activated persulfate oxidation (APO) with or without AC, is developed for the first time. Experiments are conducted to examine whether MW heating is an effective method to activate persulfate and then to decompose biorefractory organic compounds in wastewater by using an azo dye Acid Orange 7 (AO7) (up to 1000 mg/L, a nearly saturated concentration) as a model compound. The effects of chloride ion (up to 0.50 mol/L) and persulfate on MW-APO are investigated. The UV-Vis spectrum during the reaction and the chemical oxygen demand (COD) removal are determined. The radical mechanism is also discussed.

1 Experimental

1.1 Material

Sodium persulfate (SPS, $\text{Na}_2\text{S}_2\text{O}_8$, 99.0%), sodium chloride (NaCl, 99.8%), methanol (MA, HPLC grade), *tert*-butyl alcohol (TBA, HPLC grade) and Acid Orange 7 (4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid, 99.0%) were purchased from Shanghai Chemical Reagent Company, China and used without purification. Commercial active carbon (AC, AP grade, Tianjin Chemical Reagent Company, China), with a particle size of 1.0–2.0 mm, was washed with dilute hydrochloric acid and distilled water in turn, and then dried at 105°C for 2 h. Double distilled water was used in all experiments. The initial pH of all solutions was unadjusted.

1.2 Reactor and procedure

A modified domestic MW furnace (800 W) was used to supply MW energy. Three holes were drilled on its top cover, with copper pipes inserted to prevent MW emission. A 500-mL Pyrex three-necked flask reactor was installed into MW furnace. Through the holes of the three copper pipes, one neck of the flask reactor was connected to a water cooling condenser, the second one was inserted into a glass rod fixed at a motor stirrer, and the third one was filled with a plug.

Degradation reactions were carried out in the flask reactor. The AO7 solution (250 mL) was added into the reactor before the reaction. The reaction time of each experiment was exactly 11 min. At given intervals of reaction, the solution was quickly sampled and cooled down to room temperature. When AC was introduced, the suspension of AC was stirred for 10 min prior to MW heating to achieve the adsorption equilibrium between AC and AO7. The samples were centrifuged and then filtered through

a Millipore filter (0.45- μm) to remove the AC particles. All comparisons were made within the same reactor and all experiments were duplicated and performed under the atmospheric pressure.

1.3 Analysis

The UV-Vis absorbance of the samples was analyzed with a Unico 2100 spectrophotometer, USA and a Shimadzu UV1206 Spectrophotometer, Japan. The degradation of AO7 was monitored by measuring the maximum absorbance at $\lambda = 484$ nm as a function of irradiation time. COD was determined according to the standard method of potassium dichromate.

2 Results and discussion

2.1 Decolorization of AO7 by MW-APO

Acid Orange 7, a commercial textile azo dye, is stable (Stylidi *et al.*, 2004), and it has been commonly used as a model compound for the degradation of dyes (Chen *et al.*, 2005; Hammami *et al.*, 2008).

Decolorization of AO7 by MW-APO is shown in Fig. 1. The initial concentration of AO7 was 20 mg/L and the initial SPS/AO7 molar ratio was 10/1. The powder of SPS is directly added into AO7 solution. In MW-APO experiments, the time is recorded as zero when we run the MW furnace. Control experiments were conducted by MW radiation heating in the absence of SPS or by SPS oxidation at 20°C. The results show that no degradation of AO7 occurs within 11 min under control. We can draw the conclusions: (1) microwave has not enough energy to break down the molecular chain of AO7; (2) the persulfate oxidation at room temperature is not effective.

Persulfate anion ($\text{S}_2\text{O}_8^{2-}$) is a strong two-electron oxidizing agent with a standard oxidation-reduction potential ($E^0 = 2.01$ V) (Liang *et al.*, 2003), which is comparable to ozone ($E^0 = 2.07$ V) and hydrogen peroxide ($E^0 = 1.78$ V). However, the reaction rate of $\text{S}_2\text{O}_8^{2-}$ with organic matter at ambient temperatures (e.g., 20°C) is very slow. Previous study has demonstrated that at ambient temperatures the

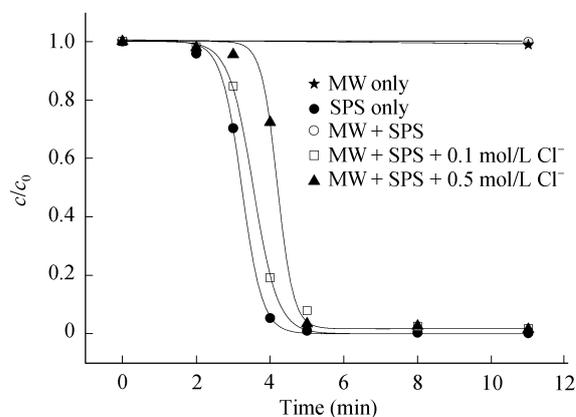


Fig. 1 Decolorization of Acid Orange 7 (AO7) by microwave activated persulfate oxidation (MW-APO) and the effect of chloride ion. The initial concentration of AO7 is 20 mg/L; the molar ratio of SPS/AO7 is 10/1. SPS: $\text{Na}_2\text{S}_2\text{O}_8$.

persulfate anion itself results in only a limited amount of TCE destruction within relatively short time period (e.g., < 6 h) (Liang *et al.*, 2007).

To our surprise, with SPS the MW-APO of AO7 is significantly rapid and 100% decolorization is achieved in about 5 min (Fig. 1). The result reveals that MW is an attractive method to activate persulfate, and thus to produce sulfate free radical $\text{SO}_4^{\cdot-}$ which is a powerful oxidant and can degrade the biorefractory organic compounds effectively. The formation of $\text{SO}_4^{\cdot-}$ by the thermal decomposition (as known "thermal activation") of the persulfate anion in an aqueous phase is shown in Eq. (1):



Under thermally enhanced conditions (i.e., temperature 30–100°C), there are considerable evidences (Dahmani *et al.*, 2006; Liang *et al.*, 2008) indicating that $\text{S}_2\text{O}_8^{2-}$ can be converted into $\text{SO}_4^{\cdot-}$ with one unpaired electron.

2.2 Effect of chloride ion

The effect of Cl^- on the degradation of pollutants is an important factor because Cl^- is ubiquitous in nature. For example, dye is a significant portion of wastewaters generated from the textile industry, and the dyeing process often requires high concentration of sodium chloride. In general opinion, the existence of Cl^- retards the degradation rate of contaminants by AOPs based on $\cdot\text{OH}$. Cl^- was believed to be an efficient scavenger to compete $\cdot\text{OH}$ (Liang *et al.*, 2006). But our group has found that the high concentration of Cl^- could greatly enhance the TiO_2 photocatalytic process of AO7, which may be due to the participation of chloride radicals (Yang *et al.*, 2005).

Therefore, the effect of high concentration of Cl^- (0.10 and 0.50 mol/L) on the decolorization of AO7 by MW-APO was determined (Fig. 1). Sodium chloride is adequately dissolved in AO7 and SPS solution before the reaction. The results show that in the presence of Cl^- , the complete decolorization is delayed for about 1–2 min. Liang *et al.* (2006) found that Cl^- has no effect on TCE degradation rate at Cl^- concentration below 0.2 mol/L, whereas at above 0.2 mol/L, TCE degradation rate was decreased with increasing Cl^- concentration.

It is widely known many kinds of wastewater have a high salinity, such as oil wastewater, landfill leachates, meat-peaking wastewater, groundwater contaminated by seawater invasion, and mining wastewater, and can not be treated easily. Our results would be useful in view of practical application of MW-APO technology.

2.3 MW-APO for high AO7 concentration

The performance of MW-APO at high concentration of AO7 was evaluated. The AO7 concentration ranged from 100 mg/L to a nearly saturated concentration 1000 mg/L. The range is much higher than commonly adopted in the attractive AOP using TiO_2 photocatalysis (20–100 mg/L) (Chen *et al.*, 2005). The molar ratio of SPS/AO7 was 50/1. The samples were diluted before the spectrum determination.

As shown in Fig. 2, the reaction is also significantly

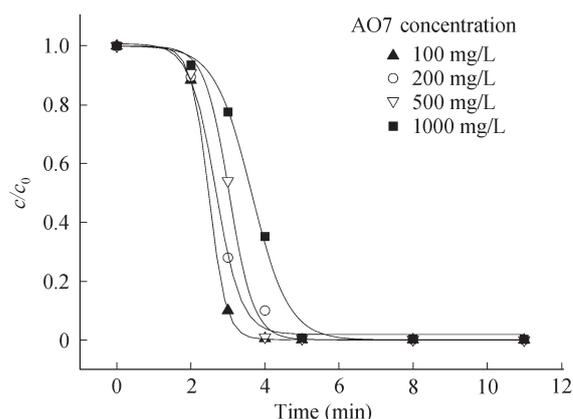


Fig. 2 MW-APO for high AO7 concentrations.

rapid and 100% decolorization is completed in only about 5–7 min. The degradation rate decreases a little while the concentration of AO7 increases by 5–50 times. Comparing with our previous study in which it needed about 4 h for 40 mg/L AO7 to decolorize 90% by using two 6 W UV lamps (λ_{max} 365 nm) and 1.0 g/L P25 TiO_2 as catalyst (Chen *et al.*, 2005), MW-APO is efficient in the degradation of dye pollutants at high concentrations.

2.4 Effect of $\text{S}_2\text{O}_8^{2-}$ concentration

The effect of $\text{S}_2\text{O}_8^{2-}$ concentration on the MW-APO decolorization at high AO7 concentrations (500 mg/L) was investigated (Fig. 3). Under the condition that molar ratio of SPS/AO7 was 10:1; 20:1; 50:1; or 100:1. The other experimental conditions were identical. It is found that the reaction rate was enhanced when the ratio increased from 10:1 to 50:1. But it seems that the cases of 50:1 and 100:1 have the almost same rate. In other words, there is no correlation between the degradation rate and the amount of $\text{S}_2\text{O}_8^{2-}$.

2.5 Catalysis of activity carbon

MW assisted catalytic wet air oxidation process was applied once to treat high concentration of *p*-nitrophenol using AC as catalyst (Bo *et al.*, 2006). In this study, the experiments of MW-assisted oxidation at relatively high AO7 concentration (500 mg/L) with AC were carried out. After

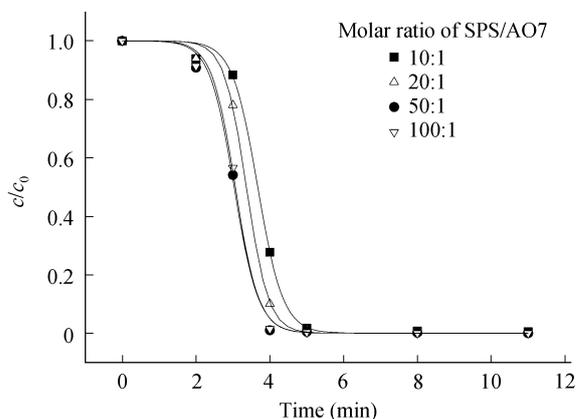


Fig. 3 Effect of $\text{S}_2\text{O}_8^{2-}$ (SPS) concentration on the decolorization of AO7 by MW-APO.

the adsorption between AC and AO7 reached equilibrium (15 min), the MW furnace was run and the reaction was started. It is found that the degradation efficiency of AO7 by MW energy (without SPS) maintains at about 10% with 0.10 g/L AC and about 50% with 1.0 g/L AC after about 5 min (Fig. 4). The degradation may be due to the generation of $\cdot\text{OH}$ in aqueous solution by MW energy by using AC as catalyst and its potential in the removal of persistent organic substances was investigated by Quan *et al.* (2007).

As shown in Fig. 4, the reaction was enhanced in the presence of AC. Especially, in the case of 1.0 g/L AC, the 100% decolorization was completed within 3 min. With the catalysis of AC, MW-APO shows a rather powerful capability to destroy dye pollutants of high concentration.

When comparing the case of AC-MW oxidation with the case of AC-MW-APO, it can be concluded that the role of persulfate in the dye degradation is significant. In AC-MW-APO, many synergistic functions would be produced. First, AC is a good sorbent for dye molecule in solution and the condensed dye would be more easily degraded. Second, AC could function as an excellent catalyst as Quan *et al.* (2007) proved in MW catalytic oxidation. Third, the generation of $\text{SO}_4^{\cdot-}$ by MW heating-activation of persulfate would play an important role. Fourth, $\cdot\text{OH}$ would also be generated. Simultaneously, other process might occur. It would be a very interesting subject for our further exploration.

2.6 UV-Vis spectrum

In all the experiments discussed above the intensity of the visible light chromophore band of AO7 (azo-linkage, 484 nm) have to be determined. The bands in the ultraviolet region, located at 228 and 310 nm, correspond to $\pi - \pi^*$ transitions in benzoic and naphthalene rings of AO7, respectively. Now we need to know whether the bands at 228 and 310 nm are destroyed by MW-APO. Experiments were carried out to examine the UV-Vis spectra of reaction solution as a function of time (Fig. 5). It is clear that the degradations of benzene ring and naphthalene ring were also rapid by MW-APO. After 11 min, the bands of AO7 in both visible and ultraviolet regions disappeared.

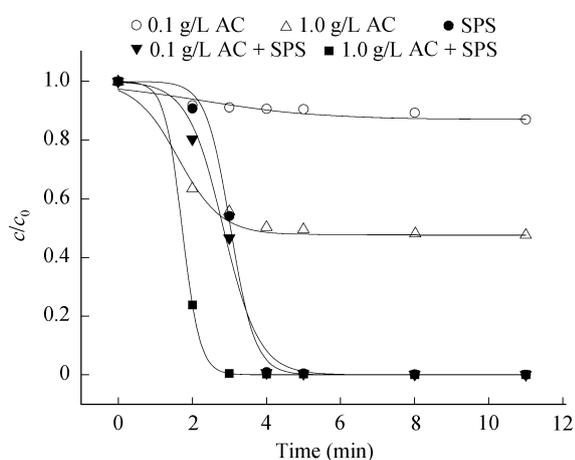


Fig. 4 MW-APO of AO7 with and without active carbon (AC). The initial concentration of AO7 is 500 mg/L; the molar ratio of SPS/AO7 is 50/1.

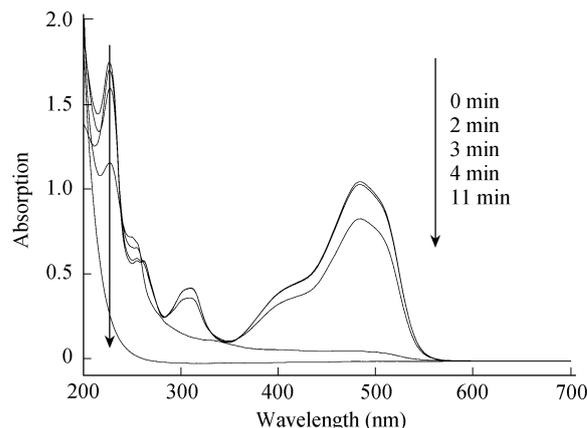


Fig. 5 UV-Vis spectra of AO7 solution as a function of time of MW-APO reaction; the initial concentration of AO7 is 20 mg/L; the molar ratio of SPS/AO7 is 10/1.

2.7 COD removal

The removal of COD at different molar ratios of persulfate/AO7 by MW-APO was studied. The COD was determined at the end of the reactions (11 min). The experimental results show that $\text{S}_2\text{O}_8^{2-}$ could effectively remove COD of AO7 solution (Fig. 6). The COD removals are 83%, 90% and 95% at persulfate/AO7 molar ratios of 10/1, 50/1 and 100/1, respectively. It is obvious that increasing of $\text{S}_2\text{O}_8^{2-}$ dosage can improve the COD removal. The MW-APO process could rapidly and effectively remove high COD in the dye pollutant.

2.8 Radical mechanism in MW-APO

It has been well known that $\text{S}_2\text{O}_8^{2-}$ can be chemically or thermally activated to generate the intermediate sulfate free radical ($\text{SO}_4^{\cdot-}$) oxidant (House *et al.*, 1962). The presence of $\text{SO}_4^{\cdot-}$ in aqueous solution can result in radical interconversion reactions to produce the hydroxyl radical ($\cdot\text{OH}$) (Dogliotti and Hayon, 1967). Both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ have the potential to produce a rapid attack on AO7 molecule.

As shown in Fig. 7, quenching studies with specific alcohols (Methanol (MA) and *tert*-butyl alcohol (TBA)) were performed using the method reported by Anipsitakis and Dionysiou (2003) to identify the primary radical

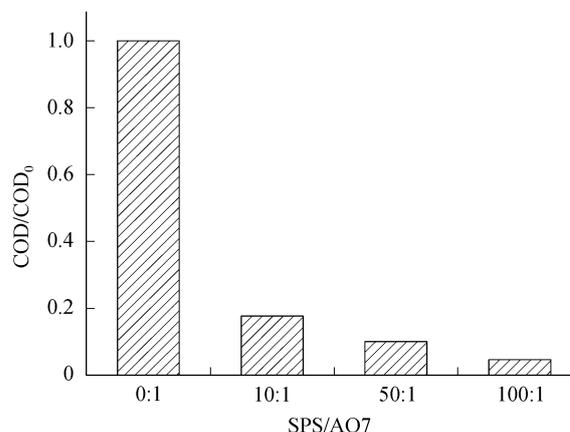


Fig. 6 COD removal at different molar ratios of persulfate/AO7 by MW-APO. The initial concentration of AO7 is 500 mg/L.

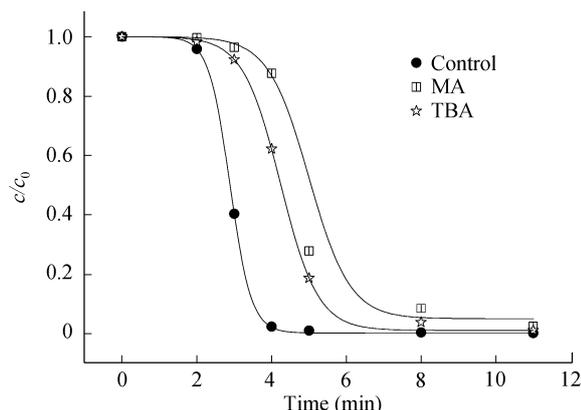
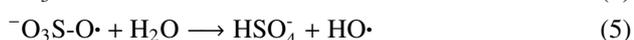


Fig. 7 Effect of alcohol (MA or TBA) on the decolorization of AO7 by MW-APO. The initial concentration of AO7 is 20 mg/L. The molar ratio of alcohol/SPS is 1000/1. MA: methanol; TBA: *tert*-butyl alcohol.

species formed in MW-APO. According to their theory, MA reacts with $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ at high and comparable rates. But TBA, which reacts much more slowly with $\text{SO}_4^{\cdot-}$, is an effective quenching agent for $\cdot\text{OH}$. Based on these properties, the experiments with MA and TBA would allow us to determine which free radical plays the dominant role after all.

In our experiments, MA and TBA are added at alcohol/oxidant molar ratio of 1000/1. The results show that the degradation rate of AO7 decreases with both MA and TBA. But the reaction with MA is restrained much greater than that with TBA. The results clearly demonstrate that both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ can degrade AO7, but $\text{SO}_4^{\cdot-}$ plays the dominant role.

The primary steps occurring in MW-APO process may be summarized as Eqs. (2)–(7). The first step is the production of $\text{SO}_4^{\cdot-}$ by MW radiation. The activation energy of the uncatalyzed reaction involving the thermal rupture of the O–O bond (Eq. (2)) was reported to be 33.5 kcal per mole (140.2 kJ/mol) (Kolthoff and Miller, 1951). Therefore, the thermal or non-thermal activation of MW may provide the required activation energy for breaking down the chemical bonds and producing sulfate free radicals. When $\text{SO}_4^{\cdot-}$ serves as an oxidant, it accepts a single electron, resulting in the production of the sulfate anion (SO_4^{2-}) (Eq. (3)). The sulfate free radical is such a strong oxidizing agent that it will mineralize numerous organic compounds to carbon dioxide and mineral acids (Wang and Hong, 1999). Thereby, generated $\text{SO}_4^{\cdot-}$ may react directly with organic molecule (Eq. (4)). On the other hand, $\cdot\text{OH}$ may be produced because of the $\text{SO}_4^{\cdot-}$ interaction with either water or hydroxyl ions (Eqs. (5) and (6)) (Chawla and Fessenden, 1975; Hayon *et al.*, 1972). The produced $\cdot\text{OH}$ may also participate in the degradation of organic molecule (Eq. (7)).



3 Conclusions

This work supplies a simple and rapid method for persulfate activation to generate $\text{SO}_4^{\cdot-}$ in aqueous solution using microwave energy. As $\text{SO}_4^{\cdot-}$ is an active and environment-friendly oxidant, it will have great significance in the fields of green chemistry, environmental protection, and other related fields.

Acknowledgments

The authors would like to thank Prof. CHEN Youyuan from College of Environmental Science and Engineering, Ocean University of China, and WANG Ping from Foreign Language School, Qingdao Agricultural University for the English revision of this manuscript.

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