Generation of hydroxyl radical in aqueous solution by microwave energy using activated carbon as catalyst and its potential in removal of persistent organic substances

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Abstract

Salicylic acid (SA, hydroxybenzoic acid) was used as molecular probe to determine hydroxyl radical ($^\bullet$OH) in aqueous solutions, where microwave (MW) radiation was involved and activated carbon (AC) existed. Rapid reaction of $^\bullet$OH with SA produced a stable fluorescence product, 2,3-dihydroxybenzoic acid (2,3-DHBA) as well as its homologue, 2,5-DHBA, which were determined by HPLC. Dose of AC, air supply, and MW power proved to be key factors influencing $^\bullet$OH generation under MW radiation. The rate of $^\bullet$OH generation reached 0.036 μmol s^{-1}, and the $^\bullet$OH yield reached 3.2 μmol in 3 min under a given condition. $^\bullet$OH is an active species with high oxidative activity and can initiate free radical reactions. Another experiment was carried out to confirm that organic substance may degrade in aqueous solution by the MW assisted catalytic process. Pentachlorophenol (PCP) was used as target. Results showed that nearly 72–100% degradation (corresponding to 40% and 82% TOC removal) was observed in 60 min for two levels of PCP concentrations (500 and 2000 mg L^{-1}), which implies that continuous production of $^\bullet$OH during MW radiation supports free radical reactions that benefit PCP degradation.
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1. Introduction

The investigation on functions and mechanisms of hydroxyl radical ($^\bullet$OH) has attracted more and more attentions because its active reactivity in a number of chemical and biological reactions, which occur in the natural and artificial processes [1,2]. The existence of $^\bullet$OH in the aquatic systems and the atmospheric phase has been universally believed [3,4]. Its existence in the environment can greatly influence the fate of many natural and artificial substances that co-exist [5]. AOP (advanced oxidation processes) is an example of the artificial processes, which were specially designed to utilize mainly $^\bullet$OH species for decomposition of non-biodegradable organic substances. In a conventional AOP process, oxidizing agents, such as H_2O_2 and O_3 are applied. They can induce the generation of $^\bullet$OH and other oxidative free radicals in the presence of catalysts or UV light. These oxidative free radicals have strong capacity to oxidize organic substances even into the degree of mineralization. However, these processes are not suitable for the treatment of heavily contaminated water.

Wet air oxidation (WAO) or called catalytic wet air oxidation (CWAO) in the case of catalysts presence, is another effective and extensively used process to treat heavily polluted industrial effluents. The apparent characteristic of the process is that oxygen comes from the air, and used as oxidant source. The oxygen can induce reactions of free radicals (such as $^\bullet$OH) under high temperature (150–350 °C) and high pressure (5–20 MPa) [6]. In the ideal case, oxidation of organic compounds would only produce CO_2, H_2O, N_2 and other mineralized substances. However, WAO or CWAO is restricted in practical application due to its severe operation conditions and high operation expenses.

Microwave (MW) is an energy composed of an electric field and magnetic field. It is a form of electromagnetic waves with the wavelengths of 1 mm–1 m (frequency 300 MHz–300 GHz) [7]. The electric field interacts with polar materials and the magnetic field reacts with magnetic or charged materials. In recent years, the enhancement of chemical reactions by MW energy

has become a very attractive method in synthetic organic chemistry because of its great capability to accelerate reactions and to improve yields and selectivity [8]. MW has also been found its application in the environmental field. Abramovitch et al. proved the rapid decompositions of polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) in soils under the existence of MW absorption or conduction materials [9,10]. In the processes, thermal cracking, caused by locally super-heating by MW energy around MW absorption or conduction materials, was possibly a dominating mechanism. MW energy was reported to enhance the generation of $^{\bullet}OH$ in aqueous solution irradiated by UV light [11]. We believe that UV, not MW induced $^{\bullet}OH$ because UV has the energy of 4.1 eV, which can cause chemical bond cleaving, while MW has only of 10^{-3} eV [12], which is not sufficient to cleave chemical bonds. However, proper designs of experiments are foreseen to be possible to generate $^{\bullet}OH$ indirectly in an aqueous solution using MW energy with the presence of proper material that has excellent capability for MW absorbing and converting it to heat. The realization of this consideration may find its significance in the fields of green chemical synthesis and pollution control. For example, we can perform CWAO process more rapidly under milder condition (low bulk temperature and even under normal pressure) using MW assisted method.

The objectives of this work are to investigate the feasibility of $^{\bullet}OH$ generation in aqueous solution using MW energy as sole energy source, and to determine the factors associated with its generation, as well as its role in the treatment of non-biodegradable organic wastewater.

Because $^{\bullet}OH$ has extremely short lifetime ($<10^{-3}$ s) [13], it is difficult to determine it directly. In this paper, salicylic acid (SA, *o*-hydroxybenzoic acid) was chosen as molecular probe to capture $^{\bullet}OH$. When $^{\bullet}OH$ exists in the solution, it will rapidly react with SA and produce 2,3-dihydroxybenzoic acid (2,3-DHBA) or 2,5-DHBA [14], which can be determined by high performance liquid chromatography (HPLC) and fluorescence detection. The (2,3-DHBA) and 2,5-DHBA yields may indicate the amount of $^{\bullet}OH$ in the solution. The reaction equation is as follows.
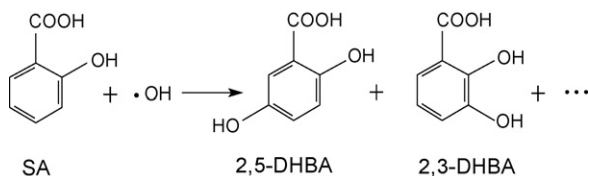
2. Experimental

2.1. Reactor system

A modified MW furnace (Whirlpool Model T120, 1000 W, China) was employed as MW source. A Ø 50 mm hole was drilled on its cover, with a copper pipe (Ø 40 mm × 50 mm) inserted to prevent MW emission [15]. The quartz column reactor (Ø 32 mm × 350 mm) was installed into MW furnace through the hole of the copper pipe, and the top of the column was connected to a vertical water cooling condenser. A bottle, charged
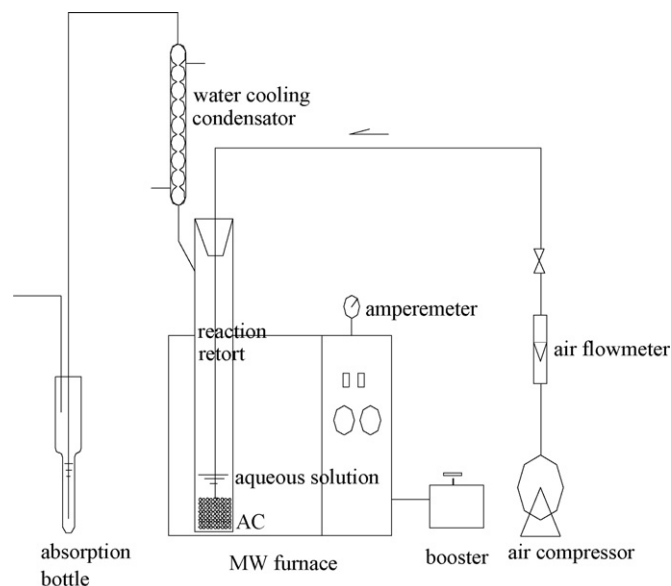

Fig. 1. Experimental setup.

with 10 mL distilled water was used to absorb the off gas after condensation. Air compressor was used to supply air. The experimental setup is shown in Fig. 1. Clearly, all experiments were performed under the atmospheric pressure.

2.2. Materials and experimental procedures

Commercial activated carbon (AC, A.P, 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.

SA (99.5% purity, from Shanghai Chemical Reagent Company, China,) was purified by recrystallizing it twice for decreasing background response during determination. 2,3-DHBA (Sigma) and 2,5-DHBA (Sigma) were prepared as standard solution according to desired concentration.

Twenty millilitres of distilled water and 10 g fresh AC were added into the reaction retort and pre-irradiated for 5 min under MW power of 800 W and airflow rate of 0.5 mL min^{-1}. Then 5 mL of 4 mmol L^{-1} SA solution was added into the retort from its top carefully, and irradiated further for a given time. Afterwards, the aqueous phase and AC were spilled from the retort and collected separately.

2.3. Analysis

After measurement of the solution volume, DHBA (representing 2,3-DHBA and 2,5-DHBA) and in the aqueous solution was determined directly by HPLC.

DHBA and SA on AC were collected using following procedure. Used AC was heated at 105 °C to constant weight. After cooling to room temperature, it was accurately weighed. DHBA and SA in the AC were extracted by 30 mL mixture of acetone and methanol (3:2, v/v), with 0.5 mL of 37% hydrochloric acid. The extraction procedure was repeated twice. The extracts for each extraction were combined and evaporated in water bath at

70 °C to dryness. The residual was dissolved in 10 mL distilled water for HPLC analysis.

Determination of SA, 2,3-DHBA and 2,5-DHBA concentrations in the solution was performed by HPLC (Agilent), coupled with fluorescent detector at 237 nm of excitation wavelength and at 405 nm of emission wavelength, using a ZORBAX Edipse XDB-C8 column (5 µm, 4.6 mm × 150 mm), with mobile phase of HAC–NaAC (30 mmol L^{-1}, pH 4.9) at flow rate of 1.0 mL min^{-1}.

The temperature was recorded with a sheltered type-K thermocouple probe.

Procedures for extraction of Pentachlorophenol (PCP) from the solution and the AC were similar to those for DHBA except that the extracting solvent was changed to mixture of acetone and dichloromethane (3:2, v/v). Determination of PCP concentrations was performed by HPLC using a Kromasil ODS (5 µm, 4.6 mm × 250 mm) reverse phase column, a methanol:water = 0.8:0.2 mL min^{-1} of the mobile phase and UV detector (220 nm). A TOC analyzer (Shimadzu TOC-V$_{CPH}$) was employed to investigate the degree of PCP mineralization.

3. Results and discussion

3.1. Identification of •OH

In HPLC chromatograph of aqueous solution after 10 s MW radiation under existence of 20 g AC and 0.5 L min^{-1} air supply, besides SA peak at the retention time of 6.48 min, two obvious peaks appear at 1.19 and 2.41 min, which were identified to be 2,3-DHBA and 2,5-DHBA by comparing their retention times with those of 2,3-DHBA and 2,5-DHBA standards under the same HPLC operation condition. The pattern of HPLC chromatograph is similar to that found in Ref. [16], where •OH was identified in UV/H$_2$O$_2$ system using the same molecular probe as we did. As it well known, the capability of UV/H$_2$O$_2$ process to generate •OH is universally believed.

Other oxidative species that might exist in the aqueous solution, such as HO$_2$, O$_3$, and H$_2$O$_2$, are difficult to realize quick reactions with SA [17]. Thus, we can believe that all 2,3-DHBA and 2,5-DHBA resulted mainly from the oxidation of SA by •OH.

3.2. Key factors for •OH generation

Experiments were carried out under following conditions in order to identify key factors for •OH generation: (1) MW irradiation alone; (2) irradiation with airflow (without AC); (3) irradiation with AC (without airflow); (4) irradiation with AC and airflow. Total yields of DHBA (2,3-DHBA + 2,5-DHBA) during whole course of radiation for four experiments were illustrated in Fig. 2. According to initial test, SA and DHBA decomposed after 5 min MW radiation. Therefore, we adapt and present here the data before 3 min (180 s).

As can be seen in Fig. 2, for the experiment (1) (MW irradiation alone) and (2) (irradiation with air supply), no •OH was produced. For the experiment (3) (MW irradiation with presence of AC) •OH was detectable but at very low level, and maintained
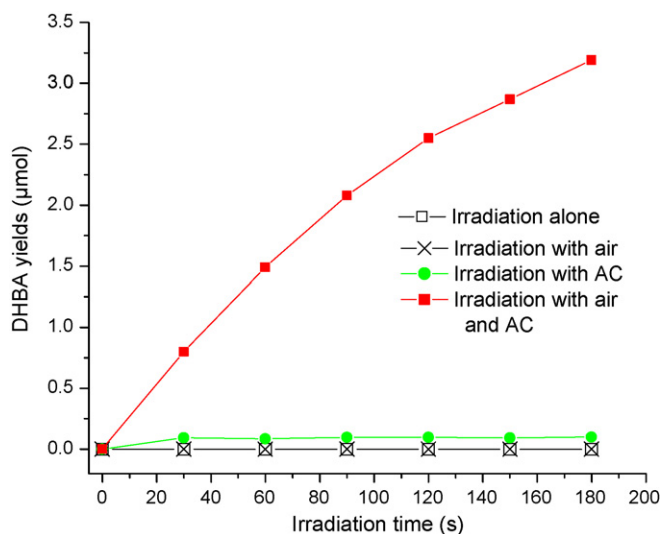

Fig. 2. Amount of DHBA generation vs. irradiation time.

a relative constant value after 30 s of irradiation. On the contrary, under the condition of AC presence and air supply, •OH generated rapidly with the increase of irradiation time. After 180 s irradiation, DHBA accumulation reached as high as 3.2 µmol. The results of above four experiments indicated that simultaneous presence of AC, air supply, and MW irradiation is essential for •OH generation. Slight generation of •OH in experiment (3) is due to the fact that limited amount of dissolved oxygen (8.2 mg L^{-1}) existed in the solution. Further discussion on the functions of AC, air supply, and MW power is as follows.

3.2.1. Activated carbon

It is clear that AC played an important role in the generation of •OH in MW involved process. Fortuny et al. proved that AC could function as excellent catalyst in CWAO [18]. Its catalytic activity was found to be eight times higher than a commercial copper oxide catalyst in CWAO for phenol degradation. It was well known that free radicals dominate in the reactions of CWAO. Therefore, it is reasonable to suppose that one function of AC should be catalytic effect on •OH generation. Another apparent characteristic for AC in MW field is its excellent capability for MW energy absorption. The MW energy absorbed by AC may quickly convert to heat, resulting in rapid increase of temperature in AC body. An experiment was carried out to compare temperature rising between dry AC and water at 800 W MW power. As shown in Fig. 3, the temperature of 20 mL water increased steadily to 103 °C (boiling point) in 25–30 s, and maintained this temperature afterwards. Water was in the boiling state, and the evaporation vapor was cooled down, flowing back to the bottom of the reactor. However, the temperature of 10 g dry AC reached as high as 800 °C in the same period of time and rose to 1200 °C within 40 s. We can imagine when 10 g AC and 20 mL water were mixed and irradiated by MW, AC could be cooled down by water. However, there should be a temperature gradient from AC particles to water phase although it is difficult to be measured. In other words, the temperature of the microsurfaces of AC particles might be high enough to induce catalytic
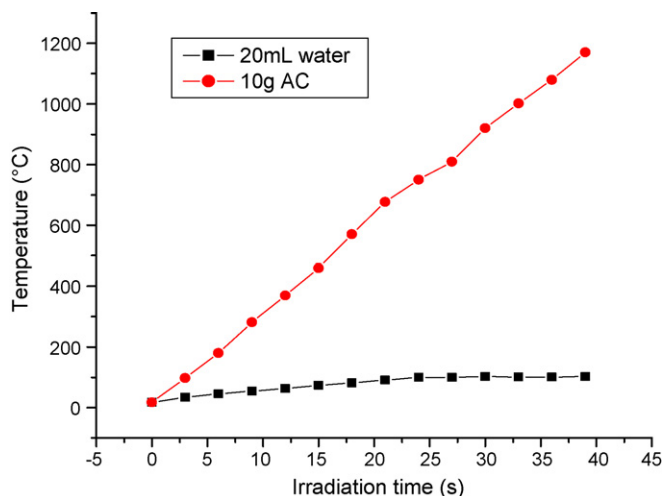
Fig. 3. Temperature records for AC and water during MW irradiation.

Fig. 5. Influence of AC dose on DHBA yields (800 W of MW power and 0.5 L min^{-1} of air flow).

generation of $^{\bullet}$OH. Similar suggestion was made by Booske et al. [19], who assumed that a portion of MW energy could be concentrated into hot spots by the localized resonant coupling of MW energy to point defects or weak surface bonds of solid materials. The "hot spots" here could benefit the initiation of free radical generation.

We expected that AC dose could have effect on $^{\bullet}$OH generation. Four different AC doses, 5, 7.5, 10, and 12.5 g, were experimented, and the temperature was recorded simultaneously (Fig. 4). The temperature for AC + water mixed phases rose faster than for water alone. The more AC dosed, the faster the temperature rose. The time to boiling (103 °C) was observed to be 28, 24, 21, 19, and 17 s, corresponding to AC dose 0, 5, 7.5, 10, and 12.5 g, respectively. Fig. 5 illustrates DHBA yields under different AC dose. It indicated that DHBA yield rose as AC dose increased. However, the differences of DHBA yields became smaller as AC dose increased from 5 to 12.5 g although the steps of AC increase remained the same (2.5 g). There is no obvious difference of DHBA yields between 10 and 12.5 g
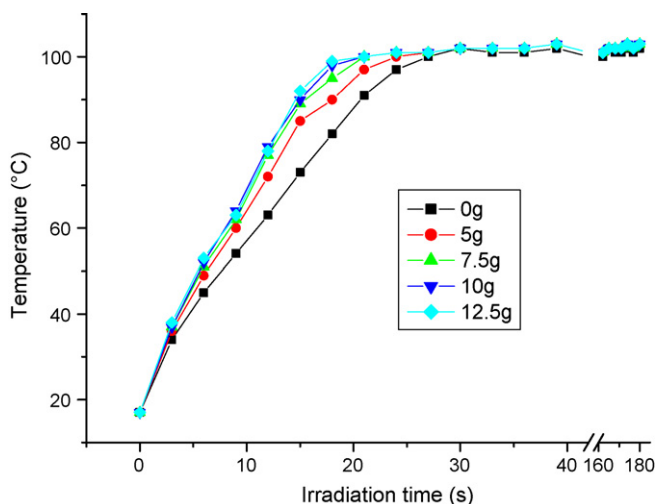
AC dose. It infers that there is an optimal AC dose for a given experimental condition.

3.2.2. Air supply

$^{\bullet}$OH generation was highly dependent on air supply (or other source of oxygen). Oxygen acts as an electron acceptor and may involve in the initial reaction. Fig. 6 shows change of DHBA yields along with the variation of air flow. Three levels, 0.2, 0.5, 0.8 L min^{-1}, were investigated. Air was supplied to the reactor using an air compressor during whole course of MW irradiation under ambient temperature and pressure. Continuous air supply supported the continuous $^{\bullet}$OH generation. Slight air supply to the aqueous solution promoted DHBA production obviously. However, excess amount of air supply showed less effect on $^{\bullet}$OH generation. For present study, about 0.5 L min^{-1} was sufficient. We can deduce that other electron acceptors such as H_2O_2 and O_3, may have similar function as oxygen for free radical generation in MW involved catalytic process.

Fig. 4. Temperature records for mixed phase of AC and water (20 mL) at different AC dose.
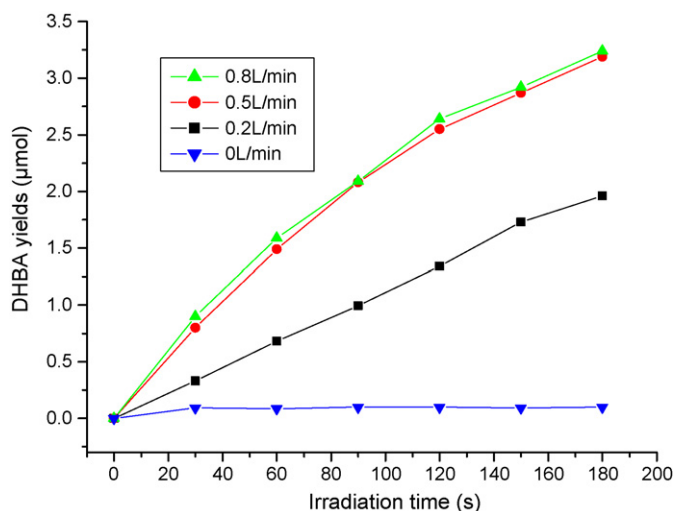

Fig. 6. Influence of airflow on DHBA yields (800 W of MW power and 10 g of AC dose).
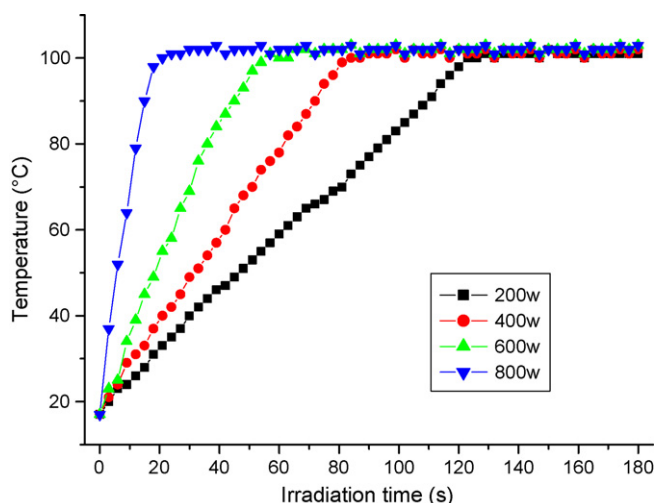
Fig. 7. Temperature records for mixed phase of AC (10 g) and water (20 mL) at different MW power.

3.2.3. MW power

MW supplied energy to the reaction system. Therefore, the positive effect of MW power output on the generation of $^\bullet$OH was foreseen. Four levels of MW power output, 200, 400, 600 and 800 W were investigated, respectively, and the temperature of the reaction phase was measured simultaneously (Fig. 7). It was found that the temperature rose to the boiling point (103 °C) at different rate under different MW power. The rate of temperature increase was measured to be 5, 2, 1.2, and 0.83 °C s^{-1} with respect to the MW power 800, 600, 400, and 200 W. Correspondingly, increase of MW power enhanced $^\bullet$OH generation. It is interesting that when MW power output increased four times from 200 to 800 W, the DHBA yield increased by the same factor of 4 (0.8–3.2 μmol) (Fig. 8). This result is very similar to that observed by Horikoshi et al. when they investigated degradation of Rhodamine-B (a dyestuff) by the integrated MW/UV method [20]. They found that color fading increased by a factor of 1.3 as MW power output increased from 225 to 300 W (300/225 = 1.3).
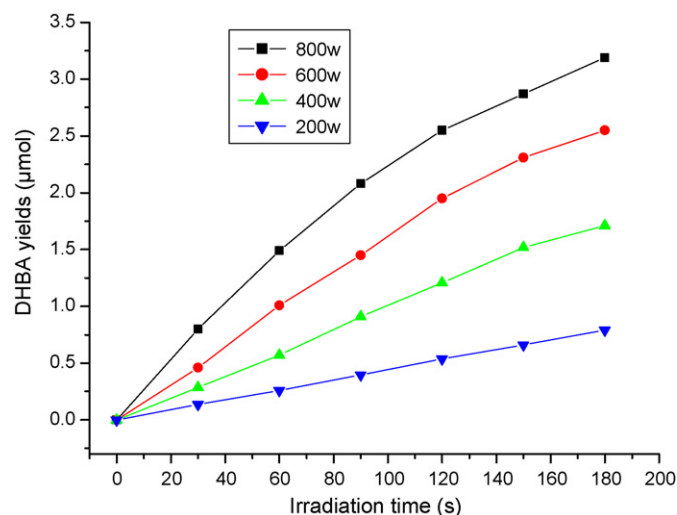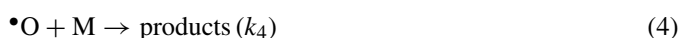

Fig. 8. Influence of MW power on DHBA yields (10 g of AC dose and 0.5 L min^{-1} of air flow).

3.3. Consideration of kinetics and mechanism for $^\bullet$OH generation

As proposed for CWAO by Tufano [21], a simplified model can be proposed to describe basic pathway to produce $^\bullet$OH in the MW involved process. As shown in Fig. 2, existence of oxygen is critical in $^\bullet$OH generation. We found that $^\bullet$OH could not be produced without oxygen supply. Therefore, it is reasonable to suggest that oxygen was involved in the first step. Based on this basic assumption, the following four simplified steps with respect to $^\bullet$OH generation and elimination were proposed:

$$O_2 \rightarrow {}^\bullet O + {}^\bullet O \, (k_1) \tag{1}$$

$$^\bullet O + H_2O \rightarrow 2\,^\bullet OH \, (k_2) \tag{2}$$

$$^\bullet OH + M \rightarrow products \, (k_3) \tag{3}$$

$$^\bullet O + M \rightarrow products \, (k_4) \tag{4}$$

where M represents the substances that can eliminate $^\bullet$OH. The catalysis of AC and MW energy demand are mainly involved in step (1). According to the reactions (1)–(4), free radical generation rates are described as follows:

$$\frac{d[^\bullet OH]}{dt} = k_2[^\bullet O][H_2O] - k_3[^\bullet OH][M] = k_2'[^\bullet O] - k_3'[^\bullet OH] \tag{5}$$

Suppose that H_2O and M exist in constant quantities, $[H_2O]$ and k_2 can be combined to a new constant k_2', and [M] and k_3 is combined to k_3'.

At steady state of $^\bullet$OH concentration, $k_2'[^\bullet O] - k_3'[^\bullet OH] = 0$, namely:

$$[\cdot OH] = \frac{k_2'}{k_3'}[\cdot O] \tag{6}$$

Similarly, we can deduce from reactions (1)–(4), the $[^\bullet O]$ concentration at steady state:

$$[^\bullet O]_{ss} = \frac{k_1'}{k_2' + k_4'} \tag{7}$$

where k_1', k_2', k_3', and k_4' represent $k_1[O_2]$, $k_2[H_2O]$, $k_3[M]$ and $k_4[M]$, respectively.

$[^\bullet OH]$ at steady state is obtained by combining Eqs. (6) and (7):

$$[^\bullet OH]_{ss} = \frac{k_1' k_2'}{k_3'(k_2' + k_4')} \tag{8}$$

Although Eqs. (1)–(8) are very helpful for understanding the theoretic pathway with respect to $^\bullet$OH generation, it is difficult in practical use because of the difficulty to determine each individual rate constant (k). In fact, determination of the apparent rate constant based on the overall equation of is a more common way for kinetic description. In present study, DHBA was formed from SA under MW irradiation and a constant supply of air. Thus, the overall equation of the reaction was expressed as:
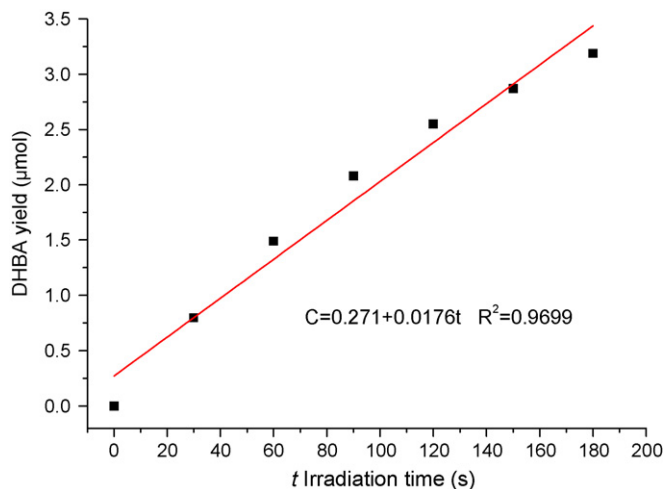
$$x SA + y O_2 + z H_2O \rightarrow a\ DHBA + other\ products\ (if\ any). \tag{9}$$

Fig. 9. Pseudo-zero-order kinetic curve of DHBA formation (800 W of MW power, 10 g of AC dose and 0.5 L min^{-1} of air flow).

The rate of DHBA formation was:

$$\frac{d[DHBA]}{dt} = k_d[SA]^x[O_2]^y[H_2O]^z \tag{10}$$

where k_d is the rate constant for DHBA formation. Since O_2 was supplied at a constant flow, and H_2O remained almost the same quantity, $[O_2]$ and $[H_2O]$ were supposed to be constant. In addition, the last item [SA] was also supposed to be constant at the initial course because excess amount of SA (20 μmol) was added. Then, the equation was simplified as:

$$\frac{d[DHBA]}{dt} = k'_d \tag{11}$$

$$[DHBA] = k'_d t + a \tag{12}$$

where k'_d is a renewed rate constant for DHBA formation. Eq. (12) expresses a linear relationship between the DHBA concentration and the irradiation time.

Fig. 9 illustrates the experimental curve for DHBA yield vs. the time of irradiation. The experiment was carried out under the condition: 10 g AC dose, 0.5 L min^{-1} air flow, and 800 W MW power. The experimental result showed good agreement with the pseudo-zero-order kinetic equation although the experimental points go slightly down in the last course, which was possibly caused by an apparent consumption of SA during the

last course, leading to non-constant for item [SA]. The rate of DHBA formation, known from the pseudo-zero-order kinetic equation, was 0.0176 μmol s^{-1}. The total DHBA yield reached 3.2 μmol in 3 min, which imply that not less than 3.2 μmol •OH were generated in the same period (production of 1 mol DHBA consumes the same amount of •OH). The fraction of •OH in the formation of DHBA was calculated from following equation:

$$fM_{•OH} = M_{DHBA} \tag{13}$$

where f stands for the percentage fraction of DHBA, M_{DHBA} the mol fraction of •OH for DHBA formation, and $M_{•OH}$ is the total amount of •OH generated. According to the literature presented by Chen and Mopper and Grootveld and Halliwell [16,22], f ranges from 50% to 90% in SA aqueous solution. Hence, the total yield of •OH was estimated to be 3.6–6.4 μmol, and the average rate was 0.020–0.036 μmol s^{-1}.

3.4. A case for degradation of persistent organic substances in aqueous solution using MW assisted oxidation method

Because MW energy has the capability to produce •OH under presence of AC and oxygen supply as shown in previous section, we expect that this MW involved method should be effective in degradation of non-biodegradable organic substances. Since air was employed as oxidant in this process, we may call it MW assisted catalytic wet air oxidation (MW/CWAO). Pentachlorophenol (PCP) was used as target substance because it is one of the typical persistent toxic substances that are hardly biodegradable.

Experiment was carried out for two levels of PCP concentration (500 and 2000 mg L^{-1} at pH 10) under the condition of MW power 800 W, airflow 0.5 L min^{-1}, and AC dose 10 g, 20 mL of PCP aqueous solution. The results were illustrated in Fig. 10.

The novel MW/CWAO showed effective degradation of PCP within 1 h of operation time. PCP removal reached nearly 100% for 500 mg L^{-1} PCP solution and 72% for 2000 mg L^{-1} PCP solution, among which 82% and 40% were mineralized, respectively. This result was comparable to the level treated using conventional CWAO, whereas, the MW/CWAO was operated under normal pressure and 100–103 °C. Therefore, the advantage of MW/CWAO over conventional CWAO in reducing operation risk is apparent.
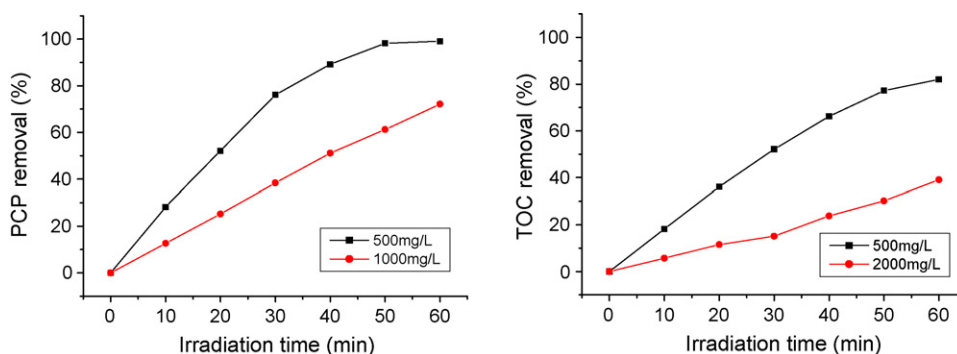

Fig. 10. PCP and TOC removal along with the MW irradiation course (condition: 800 W of MW power, 10 g of AC dose and 0.5 L min^{-1} of airflow).

4. Conclusions

$^\bullet$OH was generated indirectly by MW energy. Simultaneous presences of activated carbon and oxygen proved to be critical in $^\bullet$OH generation. Temperatures of water and AC increased at the different rates under MW irradiation due to the internal heating by MW energy, which could cause locally higher temperature in some micro-surfaces of the AC particles than water bulk. Oxygen was supposed to participate in the first step to initiate $^\bullet$OH because $^\bullet$OH was only observed when oxygen exists. Its generation was fitted for pseudo-zero-order kinetic equation at initial stage of reaction. The rate of $^\bullet$OH generation was estimated to range from 0.020 to 0.036 μmol s^{-1} under our experimental conditions. Continuous generation of $^\bullet$OH served to the degradation of pentachlorophenol, even to the degree of mineralization.

This work supplies a simple and rapid method for sequential generation of $^\bullet$OH in aqueous solution using microwave energy. As $^\bullet$OH is an active and environmental friendly oxidant, it will have great significance in the fields of green chemistry, environmental protection, and other related fields.

Acknowledgements

References

[1] K.M. Cunningham, M.C. Goldgerg, E.R. Weiner, Environ. Sci. Technol. 22 (1988) 1090–1097.

[2] R.V. Lloyd, P.M. Hanna, R.P. Mason, Free Radic. Biol. Med. 22 (1997) 885–888.

[3] B.J. Finlayson-Pitts, J.N. Pitts Jr., Science 276 (1997) 1045–1052.

[4] P.L. Brezonik, B.J. Fulkerson, Environ. Sci. Technol. 32 (1998) 3004–3010.

[5] N.H. Savage, R.M. Harrison, P.S. Monks, G. Salisbury, Atmos. Environ. 35 (2001) 515–524.

[6] F. Luck, Catal. Today 27 (1996) 195–202.

[7] X. Liu, X. Quan, L. Bo, S. Chen, Appl. Catal. A: Gen. 264 (2004) 53–58.

[8] R.S. Varma, Tetrahedron 58 (2002) 1235–1255.

[9] R.A. Abramovitch, B.Z. Huang, M. Davis, L. Peters, Chemosphere 37 (1998) 1427–1436.

[10] R.A. Abramovitch, B.Z. Huang, D.A. Abramovitch, J. Song, Chemosphere 39 (1999) 81–87.

[11] S. Horikoshi, H. Hidaka, N. Serpone, Chem. Phys. Lett. 376 (2003) 475–480.

[12] I.V. Kubrakova, J. Anal. Chem. 55 (2000) 1113–1122.

[13] J. Fossey, D. Lefort, S. Sorba, Free Radicals in Organic Chemistry, John Wiley & Sons, Paris, 1995.

[14] Y. Yoshimura, K. Otsuka, K. Uchiyama, H. Tanaka, K. Tamura, Anal. Sci. 5 (1989) 161–164.

[15] Q. Jin, S. Dai, K. Huang, Microwave Chemistry, Science Press, Beijing, 1999 (in Chinese).

[16] X. Chen, K. Mopper, J. Atmos. Chem. 36 (2000) 81–105.

[17] B.H.J. Bielski, J. Phys. Ref. Data 14 (1985) 1041–1100.

[18] A. Fortuny, J. Font, A. Fabregat, Appl. Catal. B: Environ. 19 (1998) 165–173.

[19] J.H. Booske, R.F. Cooper, I.J. Dobson, Mater. Res. 7 (1992) 495–501.

[20] S. Horikoshi, H. Hidaka, N. Serpone, Environ. Sci. Technol. 36 (2002) 1357–1366.

[21] V. Tufano, Chem. Eng. Technol. 16 (1993) 186–190.

[22] M. Grootveld, B. Halliwell, Biochem. J. 237 (1986) 499–504.