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# Efficient microwave degradation of humic acids in water using persulfate and activated carbon

Xianbing Zhang<sup>1</sup> · Zhaoxia Ding<sup>2</sup> · Juan Yang<sup>1</sup> · Leslie Cizmas<sup>3</sup> · Eric Lichtfouse<sup>4</sup> · Virender K. Sharma<sup>3</sup>

## Abstract

Humic acids are complex mixtures of organic molecules of different sizes, molecular weights and functional groups such as phenols, carboxyls, quinones and amino acids. Humic acids occur ubiquitously in media where organic matter is decomposing, such as waters, soils, sediments and organic wastes. The presence of humic acids in untreated water inhibits the oxidation of target pollutants through competing reactions and generates toxic disinfection by-products during the classical disinfection method of chlorination. There is therefore a need for alternative methods that remove humic acids. Here, degradation of humic acids at 10 mg/L was tested using 1000 W microwave irradiation assisted by 0.25–1.2 mM persulfate, with granular activated carbon at 10–50 g/L, at pH 3.0–12.0. In 90s, the highest removal of humic acids, of 75%, and humic acids mineralization, of 41%, was obtained using 1000 W microwave, 50 g/L granular activated carbon and 0.5 mM persulfate at pH 8.0. Under the same conditions without persulfate, removal was only 42% and mineralization 24%. Removal was lower than 7% using either persulfate or microwave alone. High removal with microwave, persulfate and granular activated carbon may be explained by enhanced generation of  $\text{SO}_4^-$  and  $\cdot\text{OH}$  radicals and also by better trapping/encapsulation/binding of humic acids in the granular activated carbon matrix.

**Keywords** Microwave · Sulfate radical · Granular activated carbon · Organic matter

## Introduction

Dissolved organic matter is ubiquitously present in drinking water resources. Humic acids (HA) are major components of dissolved organic matter in water and contribute to color and odor (Chen et al. 2017; Hua et al. 2017; Song et al.

2017; Lichtfouse 1997). Humic acids are a complex mixture of aliphatic and aromatic molecules of different molecular weights and functional groups (Zhou et al. 2017). Phenols, quinones, carboxyls and amino acids are common moieties in humic acids. Dissolved natural organic matter is one of the most ubiquitous substances in aquatic systems, with average concentrations in natural waters in the range from a few mg/L to hundreds of mg/L (Sillanpää et al. 2017; Wall and Choppin 2003). Concentrations of dissolved organic carbon range from 0.1 mg/L in groundwater to 50 mg/L in bogs (Stevenson 1982; Leenheer and Croué 2003). Humic substances (HS) are major components of natural organic matter in soil and water (Trellu et al. 2016). The major extractable component of humic substances in peat and grassland soils is humic acids (i.e., 70–80%) (McKnight et al. 1985). The presence of humic acids in water causes a decrease in micropollutant removal efficiency by oxidant-based methods because of competing reactions of humic acids with oxidative species (Feng et al. 2016, 2017). Additionally, when chlorine and chloramine are applied to disinfect water, disinfection by-products are generated from the reactions of moieties of humic acids with disinfectants (Heeb et al. 2014;

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Li et al. 2017; Sharma et al. 2017). Examples of disinfection by-products include trihalomethanes, haloacetic acids and haloacetonitriles, which are potentially carcinogenic (Richardson and Kimura 2016). It would be of great benefit to remove humic acids from water prior to drinking water treatment.

Microwave irradiation has been tested to determine its efficacy for degrading pollutants because of its short reaction time, high efficiency and lack of secondary pollutant generation (Kim and Ahn 2017; Liao et al. 2017a; Remya and Lin 2011a; Wang and Wang 2016). Additionally, the heating that occurs with microwave irradiation accelerates the reaction rates more than conventional heating, thereby saving energy and shortening the treatment process time (Liao et al. 2017b). For instance, the thermal effect of microwave treatment could efficiently remove volatile and semi-volatile pollutants (Wang and Wang 2016). However, microwave irradiation alone cannot degrade certain organic pollutants such as azo dyes, pharmaceuticals and pesticides (Remya and Lin 2011a, b; Waclawek et al. 2017; Wang and Wang 2016; Zhen et al. 2017). Consequently, microwave irradiation has been combined with oxidants, e.g., persulfate ( $S_2O_8^{2-}$ ) or hydrogen peroxide ( $H_2O_2$ ), or catalysts, e.g., granular activated carbon (GAC), to enhance degradation of the target pollutant (Chou et al. 2015; Gayathri et al. 2017; Remya and Lin 2011a, b, 2015).

Many studies have been conducted using either microwave-oxidant or microwave-activated carbon systems to remove target pollutants. The combination of microwave, oxidant and catalyst was previously only applied for azo dye degradation (Yang et al. 2009). This article presents for the first time the degradation of humic acids using a microwave–persulfate-activated carbon system.

The goal of this study was to design an efficient method for degrading the dissolved organic matter that contaminates waters and also interferes with procedures for drinking water treatment. To accomplish this, the degradation of humic acids was tested in water using microwave (MW) irradiation, persulfate (PS) and granular activated carbon (GAC).

## Experimental

### Materials

Analytical grade potassium persulfate was the source of persulfate and was obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Sodium hydroxide and hydrochloric acid were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All chemicals were used as received without further purification. Granular activated carbon (GAC) of 1.0–2.0 nm particle size was acquired from Gongyi LiQing

Water Purification Materials Factory, Gongyi, China. The GAC was purified before use by first washing with distilled water 5 times, followed by boiling in distilled water for 2 h. During the boiling process, the boiled water was replaced by fresh distilled water every 30 min. After boiling, the water was removed using a vacuum suction filter, obtained from Felles Photonic Instruments Company, Shanghai, China. The GAC was then dried at 105 °C for 8 h using a YH-010 drying oven with air flow, from Shanghai Yaoshi Instrument Equipment Factory, Shanghai, China. Humic acids were purchased from Sigma-Aldrich, Shanghai, China, with purity higher than 90%. A stock solution of 1000 mg/L humic acids was prepared by dissolving 1 g humic acids and 4 g NaOH in 1 L deionized water. This solution was then filtered through a 0.45- $\mu$ m Nylon 66 membrane filter from Sigma-Aldrich, Shanghai, China, before storage in the dark at room temperature.

### Experimental procedures

The microwave device used to perform these experiments was a Tangshan Nanosource Microwave from Thermal Instrument Manufacturing Co. Ltd, Tangshan, China, which had a 2450-MHz frequency and 12.2 cm wavelength. The device consisted of a self-designed microwave radiator, equipped with a temperature detection device and an Allihn condenser.

A solution containing 10 mg/L humic acids—or a total organic carbon (TOC) concentration of 7.22 mg/L—was prepared by diluting the stock solution with water obtained from a Millipore water system produced by Merck Millipore, Shanghai, China. The humic acids solution was adjusted to pH 8.0 by dropwise addition of either 0.1 M hydrochloric acid or 0.02 M sodium hydroxide. The pH was measured using an HQ40d multi-pH meter from Hach Company, Loveland, Colorado, USA. For each experiment, 100 mL of humic acid solution was transferred into a 250-mL Erlenmeyer flask and a specific amount of persulfate was added. For example, 1 or 2 mL of 50 mM persulfate stock solution was added to the sample to obtain 0.5 or 1 mM persulfate, respectively. GAC was added as appropriate. For microwave (MW)-persulfate (PS)-GAC experiments, persulfate was first added to the humic acids solution, followed by immediate addition of GAC. This mixed solution was immediately irradiated by microwave without stirring. The microwave was set so that the temperature of the mixed solution reached 97 °C in 90 s at normal pressure.

A 5-mL sample was periodically withdrawn from the conical flask using a 25-mL syringe; then, the syringe was rapidly sealed and cooled to room temperature by cold deionized water, followed by filtration with a 0.45- $\mu$ m Nylon 66 membrane filter from Sigma-Aldrich, Shanghai, China. Absorbance at 254 nm was measured in the filtered samples

using a DR6000UV-Vis spectrophotometer, from Hach Company, Loveland, Colorado, USA. The total organic carbon content was determined using the Liqui TOC analyzer from Elementar, Germany.

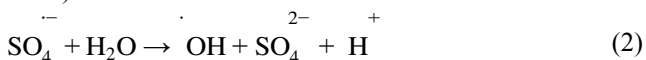
## Results and discussion

### Degradation of humic acids using microwave and persulfate

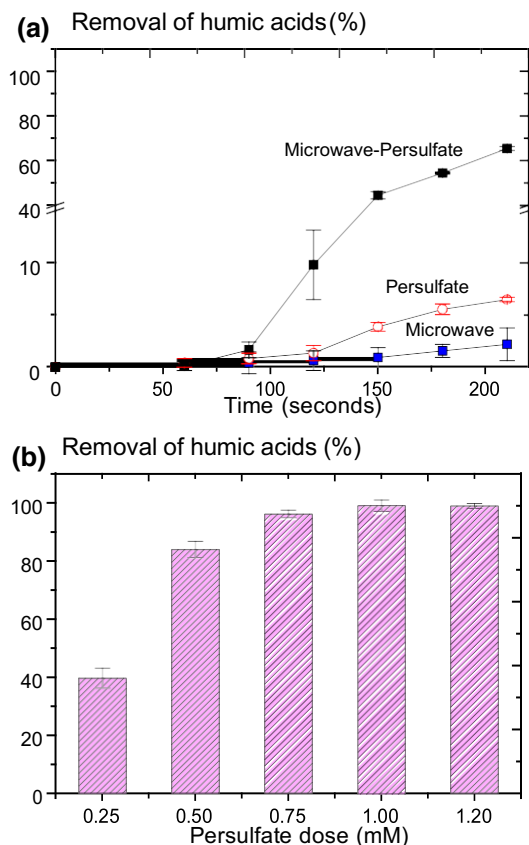
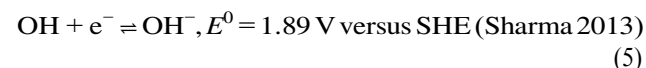
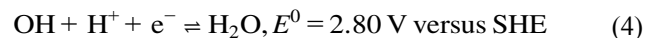
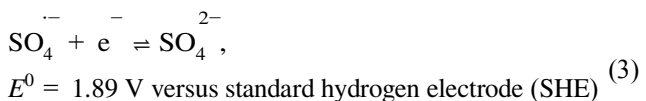
Initially, experiments using only 1000 W microwave irradiation (MW) or only 1 mM persulfate (PS) were conducted at pH 8.0. This set of experiments was followed by investigating the degradation of humic acids (HA) by 1000 W microwave irradiation (MW) in the presence of 1 mM persulfate (PS) at pH 8.0. The removal of humic acids by different processes as a function of time is shown in Fig. 1a. When the solution was treated with either microwave or persulfate alone, less than 7% of the humic acids were removed after 210 s, as indicated by a reduction in  $UV_{254}$  (Fig. 1a). When microwave was combined with 1 mM persulfate (MW-PS), the removal of humic acids increased to 67% in 210 s. In addition, with all treatments, the degradation of humic acids was observed beginning after only 60 s (Fig. 1a). These findings are explained by the temperature increase produced by microwave irradiation. In the present microwave irradiation systems (MW and MW-PS), it took about 60 s to increase the solution temperature to more than 40 °C. The low MW-reaction temperatures, i.e., 30 and 50 °C, have shown poor treatment performance for removing carbofuran (Remya and Lin 2011b). When persulfate is introduced to the MW system, the increased solution temperature generates sulfate radicals  $SO_4^-$  from persulfate:



In turn, sulfate radicals induce the formation of hydroxyl radicals ( $\cdot OH$ ) (Ghanbari and Moradi 2017; Waclawek et al. 2017):



$SO_4^-$  and  $\cdot OH$  are powerful oxidant species:



**Fig. 1** a Percentage removal of humic acids by microwave, persulfate and microwave-persulfate at pH 8.0 as indicated by a reduction in  $UV_{254}$ . Conditions: [humic acids] 10 mg/L, microwave power 1 kW, [persulfate] 1 mM, and b effect of persulfate concentration on percent removal of humic acids by microwave-persulfate at pH 8.0. Conditions: [humic acids] 10 mg/L, microwave power 1 kW, [persulfate] 1 mM, reaction time 600 s. Removal of humic acids was greatly enhanced by treatment with a combination of microwave and persulfate, compared to the results obtained with either microwave or persulfate alone. The initial persulfate concentration was important in determining the percent removal of humic acids, with optimum removal occurring with at least 0.75 mM persulfate

Both radicals can thus react with organic matter to degrade humic acids in water (Ma et al. 2018; Zhong et al. 2017).

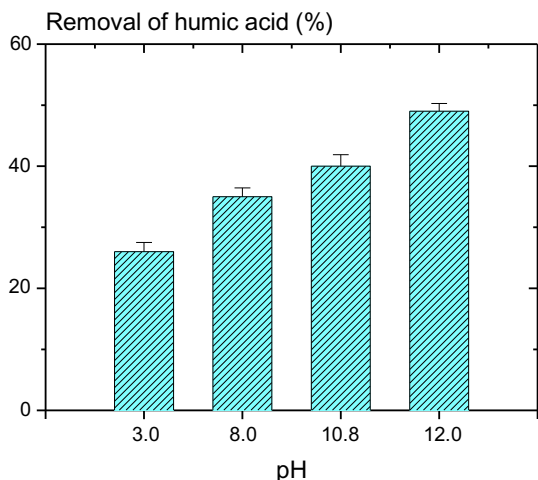
### Effect of persulfate dose on microwave-persulfate degradation of humic acids

Figure 1b shows the removal of humic acids from water during treatment with microwave/persulfate (MW-PS), with persulfate concentration ranging from 0.25 to 1.20 mM. The oxidative removal of humic acids was monitored for 600 s. Removal of humic acids increased with increasing persulfate concentration up to 1.00 mM. At 0.25 and 0.50 mM persulfate, 40 and 84% of the humic acids were removed, respectively, in 600 s. Persulfate concentrations of 0.75, 1.00 and

1.20 mM removed 96, 98 and 98% of the humic acids within 600 s, respectively (Fig. 1b). The results suggest that the initial persulfate concentration strongly affected the extent of humic acids degradation. In the MW-PS process, 0.50 mM persulfate generated substantially more reactive species than 0.25 mM persulfate, resulting in greater removal of humic acids (Fig. 1b). At 0.75 mM, 96% humic acids removal was achieved, and higher persulfate concentrations did not yield complete removal.

### Effect of pH on degradation of humic acids by microwave–persulfate

Next, the effect of pH on humic acids degradation by MW-PS was investigated by varying the solution pH from 3.1 to 12.0. As pH increased, the percent removal of humic acids increased (Fig. 2). In acidic solutions, e.g., at pH 3.0, humic acids tend to precipitate, which would inhibit the reaction between humic acids and the oxidative species generated by microwave and persulfate. The increase in the removal efficiency of MW-PS at pH higher than 7.0 may be explained by the acid–base equilibrium of humic acids moieties such as phenols, amines and amino acids (Remya and Lin 2011a). For example, in basic medium, the reactivity of  $\text{SO}_4^{\cdot -}$  and  $\cdot\text{OH}$  with constituents of humic acids increases with pH, because the basic forms of the functional groups of humic acids, i.e., the phenolate species, would react faster

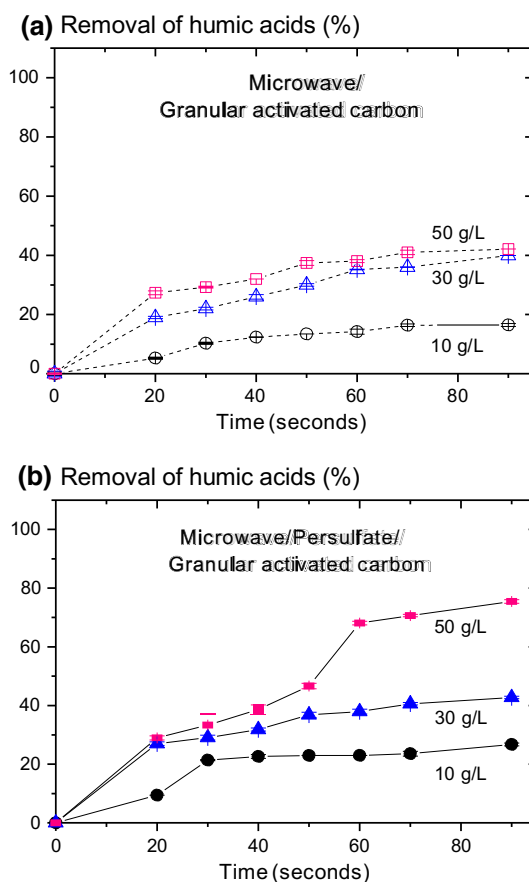


**Fig. 2** Percent removal of humic acids by microwave–persulfate in 150 s at different pH. Conditions: [humic acids] 10 mg/L, microwave power 1 kW, [persulfate] 0.5 mM. As the pH increased from 3.0 to 12.0, removal of humic acids increased substantially. The improved removal of humic acids at pH 8–12 is due to the acid–base equilibrium of humic acid moieties including phenols, amines and amino acids (Remya and Lin 2011a, b). Certain humic acid functional groups react more quickly with  $\text{SO}_4^{\cdot -}$  and  $\cdot\text{OH}$  when in the basic form, e.g., the phenolate species, rather than in the acidic form, e.g., the phenol species. (Reproduced with permission from Jasemizad et al. 2016; Villata et al. 2010; Zhong et al. 2017; Zhou et al. 2017)

with  $\text{SO}_4^{\cdot -}$  and  $\cdot\text{OH}$  than the acidic form, i.e., the phenol species (Jasemizad et al. 2016; Villata et al. 2010; Zhong et al. 2017; Zhou et al. 2017). This is consistent with the results of Fig. 2.

### Degradation of humic acids using microwave–granular activated carbon

The effect of granular activated carbon (GAC) concentration on humic acids removal was studied at pH 8.0 with either microwave (MW) alone, or with MW-persulfate (PS). The results are depicted in Fig. 3. Removal of humic



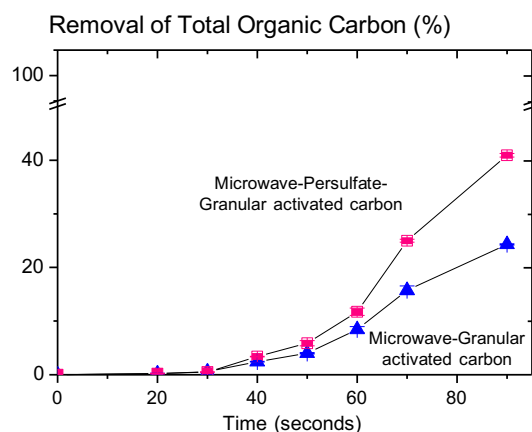
**Fig. 3** **a** Effect of granular activated carbon concentration on percent removal of humic acids (HA) at pH 8.0 by microwave–granular activated carbon only, and **b** effect of granular activated carbon concentration on percent removal of humic acids at pH 8.0 by microwave–persulfate–granular activated carbon. HA removal was quantified by measuring reduction in  $\text{UV}_{254}$ . Conditions: [humic acids] 10 mg/L, microwave power 1 kW, [persulfate] 0.5 mM, pH 8.0, [granular activated carbon] 10, 30 or 50 g/L as shown in graph. When only microwave irradiation and granular activated carbon were used, 30 g/L of granular activated carbon produced 40% humic acid degradation after 90 s, compared to only 16% humic acid degradation with 10 g/L granular activated carbon and microwave irradiation. The combined use of microwave, persulfate and 50 g/L granular activated carbon further increased humic acid degradation to 75% after 90 s

acids after 90 s increased with increasing GAC concentration following either microwave treatment alone (Fig. 3a) or microwave–persulfate (Fig. 3b). For example, following microwave irradiation with granular activated carbon concentrations of 10, 30, or 50 g/L, humic acids removal after 90 s was 16, 40 and 42%, respectively. This is explained by the fact that granular activated carbon efficiently adsorbs various organic pollutants due to its extensive porous surface area, which presents many binding sites for adsorbate species to interact with (Jiang et al. 2017; Ni et al. 2015). When MW and GAC are used together, the microwave irradiation can directly heat the inside of the GAC through permanent dipole rotation and ionic conduction loss (Wei et al. 2012).  $\cdot\text{OH}$  radical may also be found inside the GAC during MW (Bo et al. 2008; Quan et al. 2007). In the non-liquid phase, GAC absorbs microwave irradiation efficiently, producing “hot spots” with temperatures above 1000 °C (Liu et al. 2004; Lv et al. 2009; Remya and Lin 2015), leading to the increased degradation of humic acids in water. With an increase in GAC concentration, more “hot spots” were produced in the GAC, resulting in increased degradation of humic acids with increasing GAC concentration (Fig. 3a).

### Degradation of humic acids using microwave–persulfate–granular activated carbon

The use of microwave-persulfate (MW-PS) with granular activated carbon (GAC) produced substantially greater humic acids removal than MW alone with GAC. With a GAC concentration of 50 g/L, MW-PS-GAC and MW-GAC produced 75 and 42% humic acids removal, respectively, after 90 s (Fig. 3). In control experiments at pH 8.0, using MW alone, PS alone, GAC alone or MW-PS, the removal of humic acids was 0.42, 0.84, 19 and 12%, respectively (data not shown). The difference between MW-PS-GAC and MW-GAC was expected due to the production of additional oxidative species ( $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ ) in the MW-PS-GAC treatment, which enhanced the decomposition of humic acids.

Finally, to assess humic acids mineralization, total organic carbon was monitored during the degradation of humic acids by MW-GAC and MW-PS-GAC at pH 8.0 (Fig. 4). The reduction in total organic carbon indicated that humic acids mineralization occurred, resulting in loss of the mineralized product, carbon dioxide, from the solution. At 90 s, with an initial TOC concentration of 7.22 mg/L, total organic carbon removal was 24 and 41% by MW-GAC and MW-PS-GAC, respectively. The higher oxidative capacity of the MW-PS-GAC method produced greater total organic carbon removal at 90 s than the MW-GAC method (Fig. 4). However, neither process produced complete humic acids mineralization (Fig. 4). This indicates that both processes decomposed humic acids to other organic components as well as the mineralized product, carbon dioxide.



**Fig. 4** Total organic carbon (TOC) removal, indicating mineralization of humic acids by microwave–granular activated carbon or microwave–persulfate–granular activated carbon methods at pH 8.0. Conditions: [humic acids] 10 mg/L, microwave power 1000 W, [persulfate] 0.5 mM, granular activated carbon was 50 g/L, initial TOC concentration was 7.22 mg/L. Note the substantially greater humic acid mineralization at 90 s with the microwave–persulfate–granular activated carbon system

### Conclusion

The efficiency of humic acids removal in 90 s at pH 8.0 was 12% using microwave with persulfate, 42% using microwave with granular activated carbon and 75% using microwave with both persulfate and granular activated carbon. Therefore, the combination of MW-GAC-PS seems to be synergistic. This high removal with microwave, persulfate and granular activated carbon is explained by enhanced generation of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  radicals as well as improved trapping/adsorption of humic acids in the granular activated carbon.

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