Activation of peroxymonosulfate by microwave irradiation for degradation of organic contaminants

Chengdu Qi [a,b], Xitao Liu [a,*], Chunye Lin [a], Huijuan Zhang [a], Xiaowan Li [a], Jun Ma [a]

[a] State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, PR China
[b] State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Beijing Key Laboratory for Emerging Organic Contaminants Control, School of Environment, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- MW can activate PMS efficiently, especially at temperatures above 60 °C.
- BPA degradation was accelerated in real water compared to ultrapure water.
- SO_4^- and $\cdot OH$ were the dominant reactive oxygen species in the MW/PMS process.
- Degradation pathway was proposed based on intermediates identified by GC–MS.

GRAPHICAL ABSTRACT
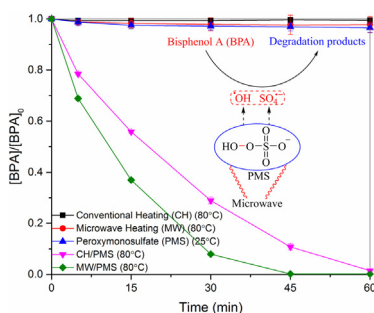
ABSTRACT

In this study, peroxymonosulfate (PMS) activation was successfully achieved by microwave (MW) irradiation directly and subsequently applied for the degradation of bisphenol A (BPA, an endocrine disrupting chemical frequently detected in the environment), especially at temperatures above 60 °C. The experiment results showed that a higher reaction temperature, MW power level, initial PMS dose, and initial solution pH had positive effects on the degradation efficiency of BPA. The degradation efficiency of BPA was slightly enhanced in real water compared to that in ultrapure water. The result of radical scavenger experiments indicated that both sulfate radical and hydroxyl radical were the dominant reactive oxygen species. Based on the results of high performance liquid chromatography and gas chromatography-mass spectrometry, several transformation pathways, including β-scission, hydroxylation, dehydration, oxidative skeletal rearrangement, and ring opening, were proposed. The complete degradation of several typical organic contaminants was also achieved using the MW/PMS process. This work would broaden the selection of PMS activation methods and provide an option for wastewater treatment.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Advanced oxidation processes (AOPs) based on persulfate activation have been comprehensively studied for the degradation of refractory organic contaminants in various media, including wastewater, groundwater, and soil [1–6]. Compared with hydrogen peroxide (H_2O_2), a vital constituent of Fenton and Fenton-like AOPs, persulfates (peroxymonosulfate (PMS) or peroxydisulfate (PDS)) exhibit superior performance, ease of storage and transport, pH-tolerance and stability [7]. Stable at room temperature, persulfates can be activated by the use of heat [8,9], transition metals [10,11], ultraviolet (UV) light [12,13], and base [14,15], generating

* Corresponding author.
E-mail addresses: qichengdu@mail.tsinghua.edu.cn (C. Qi), liuxt@bnu.edu.cn (X. Liu).

highly active species, such as the sulfate radical and hydroxyl radical.

However, UV light cannot be effectively transmitted through turbid and colored wastewater. Base activation requires large amounts of an alkaline substance to adjust the initial and final reaction system pH levels. Transition metal activation (e.g., Fe^{2+} for PDS and Co^{2+} for PMS) poses the secondary risks of metal toxicity and metal sludge accumulation.

Consequently, heat, a very attractive and controllable activation approach, has been investigated in several cases [8,13,16,17]. In addition to acting as an activator, it can increase the organic contaminants' solubility and reaction system temperature, thus increasing the reaction rates and decreasing the treatment time. Microwave (MW) heating has been proven to be superior to conventional heating in some aspects, such as its ability to accelerate reaction rates, provide selective heating, and/or suppress reaction pathways [18–20]. Furthermore, a MW activated PDS (MW/PDS) process has been successfully employed to degrade various organic contaminants, including acid orange 7 [21], methylene blue [22], reactive yellow 145 [23], sulfamethoxazole [24], pentachlorophenol [25], and perflurooctanoic acid [26] in aqueous solution.

Recently, Pang and Lei [27] reported that MW can enhance the degradation efficiency of *p*-nitrophenol (PNP) in a $MnFe_2O_4$ activated PMS process. However, no significant degradation of PNP was observed in the MW/PMS process, which may be attributed to the short contact time (less than 2 min). PMS and PDS, derivatives of H_2O_2, are similar in structure. PDS and H_2O_2 can be activated by MW and applied in organic contaminants degradation [21,28,29]. Thus, we can deduce that PMS could also be activated by MW. Furthermore, a MW activated PMS (MW/PMS) process was successfully employed to degrade the chemical oxygen demand (COD) in landfill leachate [30]. However, to the best of our knowledge, there has been no systematic research on the use of MW to activate PMS directly for the degradation of organic contaminants in water.

The objectives of this work were (1) to explore the feasibility of implementing MW for PMS activation and the application of a MW/PMS process for the degradation of bisphenol A (BPA, an endocrine disrupting chemical frequently detected in the environment); (2) to investigate the influences of several important parameters, including the reaction temperature, MW power, initial PMS and BPA concentrations, initial solution pH, and water type, on the degradation efficiency of BPA; (3) to identify the dominant reactive oxygen species involved in the MW/PMS process; (4) to propose a possible mechanism for BPA degradation; and (5) to test the performance of the MW/PMS process in degrading several typical organic contaminants in water.

2. Materials and methods

2.1. Materials

All of the chemical reagents and organic solvents were at least analytical grade and used as received without further purification. PMS ($2KHSO_5·KHSO_4·K_2SO_4$), BPA, atrazine (ATZ), sulfamethoxazole (SMX), and ibuprofen (IBP) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide, hydrogen peroxide, PDS ($Na_2S_2O_8$), sodium bicarbonate, potassium iodide, acid orange 7 (AO7), and methylene blue (MB) were purchased from Sinopharm (Shanghai, China). Acetonitrile (ACN), ethanol (EtOH), *tert*-butyl alcohol (TBA), and dichloromethane of HPLC grade were supplied by J&K Scientific (Beijing, China). All of the solutions were prepared using ultrapure water with a resistance of 18.2 MΩ·cm from a Milli-Q Integral 5 system (EMD Millipore, Billerica, MA, USA).

2.2. Experimental procedure

A stock solution of BPA (100 mg·L^{-1}) was prepared with ultra-pure water prior to each batch experiment and stirred overnight at room temperature until complete BPA dissolution. PMS stock solutions (typically 0.5 M) were prepared before use. MW heating degradation experiments were carried out in a 250-mL three-necked round-bottomed flask equipped with a reflux condenser. The temperature of the reaction mixture was measured by an immersed platinum resistance thermometer. The flask was placed on a commercial MW reactor (XH-100A, 100–1000 W, Beijing Xianghu Science and Technology Development Co., Ltd) that controlled all of the experimental conditions, including the reaction temperature, MW power, stirring speed, and reaction time. Two hundred and fifty milliliters of the BPA solution (typically 87.6 μM, 20 mg·L^{-1}) was heated in the XH-100A MW reactor with an appropriate MW power level (typically 500 W) to reach and maintain the preset temperature (typically 80 °C). The reaction was initiated once 5 mL of the PMS stock solution (typically 0.5 M) was added, except in the studies investigating the effect of the MW power. In this case, PMS and BPA were premixed and then the reaction was initiated once MW reactor is heated at different MW power levels to a preset temperature (if can reach). Typically, the degradation experiments were conducted at the natural pH of the reaction mixture (2.45), except for the studies on the effect of the initial solution pH. In such cases, the initial solution pH was adjusted to the desired values using appropriate volumes of 0.1 M NaOH or H_2SO_4. During treatment, rapid stirring (approximately 500 r·min^{-1}) with a magnet ensured a completely mixed solution state. The experiments for the degradation of AO7, MB, ATZ, IBP, and SMX were performed under identical conditions. The temperature effects with conventional heating were also investigated and compared by maintaining the temperature of the BPA solution at 40, 50, 60, 70, and 80 °C using a thermostatically controlled water bath (THZ-82A, China Jiangsu Jingtan Ronghua Instrumental Factory). At given reaction time intervals (0, 5, 15, 30, 45, and 60 min), approximately 5 mL samples were withdrawn and chilled in an ice bath for 30 min to stop the reaction, after which they were kept in a 4 °C refrigerator until further treatment and analysis. All of the experiments were carried out in duplicate.

2.3. Analytical methods

The concentrations of the organic contaminants (except AO7 and MB) were measured using high performance liquid chromatography (HPLC, Waters 2695, USA) with a Zorbax Eclipse Plus C18 column (150 mm × 4.6 mm, 5 μm, Santa Clara, CA, USA) and a UV detector (Waters 2487). The mobile phase was a mixture of ACN and water (60:40, v/v) at a flow rate of 1.0 mL min^{-1}. The column temperature was 25 °C, and the injection volume was 20 μL. Detection wavelengths of 276, 220, 264, and 222 nm were used for BPA, ATZ, SMX, and IBP, respectively. A DR6000 UV–visible spectrophotometer (HACH, Loveland, CO, USA) was employed to test the concentrations of AO7 and MB at wavelengths of 484 and 664 nm, respectively. For all of the kinetic experiments conducted under different conditions, the degradation efficiency $(1-(C_t/C_0))$ of the organic contaminants was fitted using the pseudo-first-order rate kinetic equation (Eq. (1)):

$$-\ln(C_t/C_0) = k_{obs}t \qquad (1)$$

where C_0 and C_t are the molar concentrations of the organic contaminant (μM) at time 0 and reaction time t (min), respectively; k_{obs} is the rate constant (min^{-1}).

Gas chromatography-mass spectrometry (GC–MS) was used to detect the intermediates of BPA degradation (Text S1). The PMS