Ultrasonics Sonochemistry 22 (2015) 182–187

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Sulfamethoxazole degradation by ultrasound/ozone oxidation process in water: Kinetics, mechanisms, and pathways

Wan-Qian Guo *, Ren-Li Yin, Xian-Jiao Zhou, Juan-Shan Du, Hai-Ou Cao, Shan-Shan Yang, Nan-Qi Ren

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China

ARTICLE INFO

Article history:
Received 19 May 2014
Received in revised form 7 July 2014
Accepted 8 July 2014
Available online 24 July 2014

Keywords:
Sulfamethoxazole
Ultrasound
Ozone
Kinetics
Mechanisms
Pathways

ABSTRACT

In this research, sulfamethoxazole (SMX) degradation was investigated using ultrasound (US), ozone (O_3) and ultrasound/ozone oxidation process (UOOP). It was proved that ultrasound significantly enhanced SMX ozonation by assisting ozone in producing more hydroxyl radicals in UOOP. Ultrasound also made the rate constants improve by kinetics analysis. When ultrasound was added to the ozonation process, the reaction rate increased by 6–26% under different pH conditions. Moreover, main intermediates oxidized by US, O_3 and UOOP system were identified. Although the main intermediates in ozonation and UOOP were similar, the introduction of ultrasound in UOOP had well improved the cleavage of S–N bond. In this condition SMX become much easier to be attacked, which led to enhanced SMX removal rate in UOOP compared to the other two examined processes. Finally, the SMX degradation pathways were proposed.

1. Introduction

Contamination of natural waters by pharmaceuticals and personal care products are regarded as a rising environmental issue of global concern. Among various pharmaceutical compounds, antibiotics have been found in effluents of some sewage treatment plants as well as in surface water and groundwater in USA, UK, Canada, Germany and China [1–3]. Sulfamethoxazole (SMX) was a commonly used sulfonamide antibiotic and shared a large global consumption in animal food industry. In the year 2007, SMX is the 6th most pervasively prescribed antibiotic in Canada [4]. It is one of the most commonly used antibiotics in China as well [5]. The SMX can treat the coccidiosis, diarrhea and gastroenteritis, which are the most frequently outbreaking illnesses [6]. Due to insufficient control for the past, a great deal of SMX enters into the environment per annual. Although in recent years, pollution control of discharged antibiotics and their by-products have been drawing increasing attention by the government and researchers, SMX removal rate presents low between 20% and 30% in wastewater treatment plants [7]. As a result, large amount of untreated SMX residues have caused great pollution in the surface water and underground aquifers over years. Moreover, the antibiotic residuals can lead animals and people to evolve resistant genes, which would cause antibiotics finally disabled to the diseases. Therefore, it is necessary to increase the SMX removal rate by modified and optimal treatment techniques in water treatment process.

Ultrasound (US), a promising and environmental friendly treatment technology for water and wastewater treatment, has raised a wide attention in environmental applications such as organic pollutants control [8–10], biological hydrogen production [11,12], and excess sludge reduction [13–15]. Recently, US has been frequently employed to degrade aquatic emergency micropollutants including sulfonamides and other pharmaceuticals, because the strong oxidizing hydroxyl radicals (·OH) were generated by the collapse of bubbles cavitation in water environment. Naddeo et al. [16] evaluated the US process on pharmaceuticals degradation (diclofenac, amoxicillin, carbamazepine). It was found that sonication showed potential in pharmaceuticals removal, biodegradability increment and toxicity reduction. However, the effect of US itself still needs to improve and it is uneconomical to use US alone to remove pollutants completely.

In order to achieve high efficient and economical removal of organic matters, ultrasound is a promising tool to combine with other traditional treatment technologies. In environmental protection area, ultrasound has been most widely used to combine with ozone for the removal of non-biodegradable organic contaminants [17–20]. Wang et al. [21] applied ozone combined with ultrasound for tetracycline (TC) degradation in a rectangular air-lift reactor, with high TC removal rate and increased biodegradability. However, the study only investigated the impact factors, mineralization and toxicity during SMX degradation. The degradation mechanism

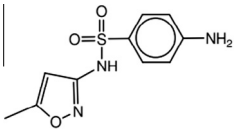
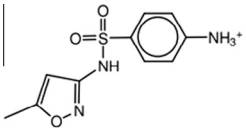
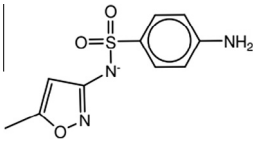
* Corresponding author. Tel./fax: +86 451 86283008.
E-mail address: guowanqian@hit.edu.cn (W.-Q. Guo).

http://dx.doi.org/10.1016/j.ultsonch.2014.07.008
1350-4177/

of pollutant was unclear, and the effect of ultrasound was not mentioned. Those subjects should not be ignored. In previous study, the ultrasonic-assisted ozone oxidation process (UAOOP) had been successfully employed for the degradation of triphenylmethane dye and the decolorization of malachite green (MG) that proposed a promising energy-saving way for refractory pollutant degradation [22,23]. The results showed that the UAOOP not only enhanced the MG wastewater decolorization rate but also saved reaction time and ozone dosage. Above all, ultrasound-combined-O_3 process is an efficient wastewater treatment technology, which improved the biodegradability of wastewater, enhanced the dye decolorization, increased COD removal rate and reduced biological toxicity. Consequently, the trials on other organic matters degradation, taking SMX for example, by ultrasound/ozone oxidation process will be feasible and promising.

Therefore, in this study, sulfamethoxazole (SMX) degradation was investigated using US, O_3 and ultrasound/ozone oxidation process (UOOP). To clarify the ultrasound enhancement mechanism on SMX degradation, experiments were designed: (1) to clarify the effect of ultrasound for SMX ozonation, by the role of ultrasound played in the UOOP system; (2) to investigate the enhancement of ultrasound for SMX removal, by the means of determining the kinetic constants under different pH through the competitive kinetics; (3) to deduce the influence of ultrasound for SMX degradation pathways, by comparing the intermediates between O_3 and UOOP system.

Table 1
Chemical structure and relevant data for SMX.

Compound	Sulfamethoxazole (SMX)
Molecular Formula	$C_{10}H_{11}N_3O_3S$
Structure	
Formula weight (g mol-1)	253.3
pKa_1	1.6
pKa_2	5.7
Protonated form	
Deprotonated form	

2. Materials and methods

2.1. Materials

Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$, analytical reagent, 99.0%) was purchased from Sigma and used as received without further purification. The structure and the relevant data of SMX were shown in Table 1. Fig. 1 showed the schematic illustration of experimental setup.

2.2. Methods

SMX solutions were buffered by the addition of adequate quantities of Na_2HPO_4, H_3PO_4 and KH_2PO_4. Oxidation experiments were carried out in a 1.5L reactor with a continuous supply of O_3. Ozone was generated using an ozone generator with gaseous flow meter (DHX-SS-1G, Jiujiu ozone, Harbin, China). Ultrasound (Shanghai Sonxi Ultrasonic Instrument, 20 kHz, 1200 W) was generated by an ultrasonic generator equipped with a titanium probe transducer 8 mm in diameter. Each run in the research was performed three times to ensure reproducibility. The gaseous product from the reactor was led to a terminator, where the remaining ozone was absorbed by KI solution.

The hydroxyl radicals were quantified by fluorescence measurement (FS-6500) [24,25]. The ·OH was trapped by the direct addition reaction with terephthalic acid (TA). The initial concentrations of TA and NaOH were set at 2 mM and 5 mM respectively. It is emphasized that the apparent concentration of ·OH only reflected the portion of ·OH that has been trapped by the TA, and was a relative measure of the real concentration of ·OH in the water.

The method applied in kinetics was based on the comparison reaction between the degradation rate of SMX and that of the reference compound. In this research, the reference compound was the fumaric acid (FA). To calculate the kinetic constant of the SMX in O_3 alone process and UOOP system, buffered solutions containing both FA and SMX with concentration of 0.5 mM L^{-1}, which were mixed and the concentrations were tested. The runs were carried out at pH 5, 7 and 9. SMX concentration was determined by HPLC (Waters, C_{18}, $\lambda = 270$ nm). The mobile phase was a mixture of acetonitrile and 0.2% acetic acid with the volume ratio 40:60. A 10 μL volume was injected using the auto sampler. FA concentration was also determined by HPLC ($\lambda = 210$ nm). The mobile phase was a mixture of acetonitrile and 0.5% phosphoric acid with the volume ratio 5:95.

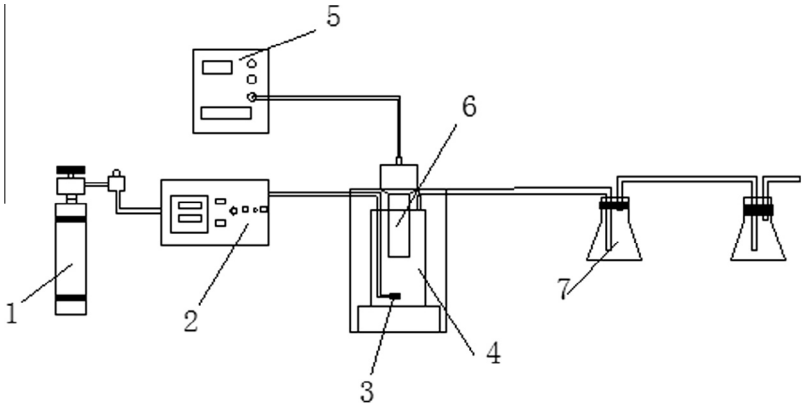


Fig. 1. The schematic illustration of experimental setup, 1 oxygen cylinder; 2 ozonator; 3 aerator; 4 reactor; 5 Ultrasonic generator; 6 ultrasonic probe; 7 gas absorption equipments.