Chemosphere 119 (2015) 326–333

Contents lists available at ScienceDirect

Chemosphere

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

Degradation of phenazone in aqueous solution with ozone: Influencing factors and degradation pathways

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HIGHLIGHTS

- The pseudo-first-order kinetic model was determined during phenazone ozonation.
- NO_3^- improved phenazone degradation rate, while other anions showed negative effects.
- Optimal H_2O_2 addition of 0.135 mM boosted the phenazone ozonation efficiency by 45.9%.
- Degradation pathways were proposed by 10 phenazone ozonation by-products.

ARTICLE INFO

Article history:
Received 25 December 2013
Received in revised form 22 May 2014
Accepted 22 June 2014
Available online 17 July 2014

Handling Editor: Shane Snyder

Keywords:
Phenazone
Ozonation
Kinetics
Degradation pathway
Toxicity

ABSTRACT

Oxidation kinetics and degradation pathways of phenazone (an analgesic and antipyretic drug) upon reaction with O_3 were investigated. Kinetic studies on degradation of phenazone were carried out under different operating conditions such as temperature, pH, anions and H_2O_2 addition. Results showed that the degradation followed the pseudo-first-order kinetic model. The reaction rate constant (k_{obs}) of phenazone reached the maximum at 20 °C (9.653×10^{-3} s^{-1}). The presence of NO_3^- could enhance the degradation rate, while the addition of HCO_3^-, SO_4^{2-}, Cl^- and the rise of pH showed negative effects on the ozonation of phenazone. H_2O_2 addition increased the phenazone degradation efficiency by 45.9% with the optimal concentration of 0.135 mM. Reaction by-products were evaluated by UPLC-Q-TOF-MS, which allowed the identification of a total of 10 by-products. The transformation pathways of phenazone ozonation consisted mainly of electrophilic addition and substitution, pyrazole ring opening, hydroxylation, dephenylization and coupling. The toxicity of these intermediate products showed that they are expected not to be more toxic than phenazone, with the exception of P7 (aniline) and P10 (1,5-dimethyl-4-((1-methyl-2-phenylhydrazinyl)methoxy)-2-phenyl-1H-pyrazol-3(2H)-one).

1. Introduction

The widespread occurrence of pharmaceuticals and personal-care products (PPCPs) in the aquatic environment has been recognized as an emerging worldwide problem. Despite dilution, partial degradation and sorption in migration and transformation process, PPCPs are frequently detected in treated water, raw water, and even drinking water (Luo et al., 2014). Although PPCPs have typically trace concentration in the ng L^{-1} to μg L^{-1} range, they may cause potential risk in drinking water on human health, due to their biologically active nature, accumulation and persistent physico-chemical properties (Verlicchi et al., 2012). In addition, conventional drinking water treatment approaches such as coagulation/flocculation, filtration has low efficiency in the removal of these substances (Mompelat et al., 2009; Capdeville and Budzinski, 2011). Phenazone (also known as antipyrine) is an analgesic and antipyretic drug, which is widely used in clinics to relieve headache, fever and general pain (e.g. ~0.35 g phenazone consumed (year. person)$^{-1}$ in Germany) (Cai et al., 2013a). Because of its biochemical-persistance, removal efficiency for phenazone in wastewater treatment plant was only ~33%, which mean sizable part of phenazone would be discharged into natural waters (Pieper et al., 2010; Verlicchi et al., 2012). Thus, phenazone has been widely detected in surface water, ground water and even drinking water at up to the μg L^{-1} level (Zühlke et al., 2004). Although there is no direct evidence for the ecotoxicity of phenazone, its EC_{50} values estimated from QSAR calculated are in the 1.10–6.70 mg L^{-1} level

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http://dx.doi.org/10.1016/j.chemosphere.2014.06.082
0045-6535/

(Sanderson et al., 2003). Based on its typical environmental concentrations and persistence, phenazone ranks among the most relevant pharmaceuticals for invertebrates and algae (Gros et al., 2010).

Because phenazone is difficult to be effectively removed by the physical processes in water treatment such as coagulation, sedimentation and sand filtration, considerable attention to the chemical techniques such as oxidation and disinfection treatments has been paid to explore the effective degradation approach. Up to now, many methods including advanced oxidation processes were carried out for phenazone degradation, and the results obtained by using Cl_2 (Rodil et al., 2012), ClO_2 (Huber et al., 2005), $S_2O_8^{2-}$ (Tan et al., 2013a), photocatalysis (UV and/or catalyst) (Pastrana-Martínez et al., 2012; Tan et al., 2013b) and O_3 (Yoon et al., 2013) has shown high activity for phenazone degradation. Ozonation has recently appeared as an important technology for the removal of most organic pollutants in water treatment, and is expected to experience fast growth in the disinfection market (Esplugas et al., 2007). Furthermore, ozonation is advantageous in drinking water treatment for a number of reasons: (1) it can both remove taste and odor compounds, organic micropollutants *etc*., and disinfect pathogenic microorganism with lower concentration in shorter contact time compared to other disinfectants; (2) it is able to enhance the efficiency of the coagulation/flocculation process during water treatment; (3) it reduces the formation potential of hazardous chlorination by-products by oxidizing their precursors. However, to the best of our knowledge, information about the phenazone ozonation is limited, especially in kinetic studies into the ozonation process at different operating parameters. In addition, even though O_3 can remove the target drugs quickly and effectively, oxidation process could not mineralize organics completely and in some cases, highly toxic by-products might be produced inevitably (Ikehata et al., 2006). These intermediates often differ in their toxicity and potential for accumulation compared to the parent compounds. Moreover, these undesired degradation by-products may be more difficult to be removed than the original compound and become new chemical entities in the environment or in the drinking water (Fatta-Kassinos et al., 2011). Therefore, evaluation and determination of by-products from ozonation are also important considerations for environmental protection purposes.

In the light of these concerns, our objective of this work was to technically evaluate the degradation of phenazone by O_3 in drinking water treatment. On the one hand, operating parameters influencing the treatment, including initial phenazone concentration, temperature, pH, and the additions of inhibitors and accelerators of ozonation were investigated from the reaction kinetics' perspective. On the other hand, the tentative degradation pathway for phenazone ozonation was proposed by identifying the transformation products during the process.

2. Materials and methods

2.1. Chemicals and reagents

Phenazone ($\geqslant$99.5%) with physico-chemical characteristics of molecular weight 188.23, log K_{ow} 0.38 and density 1.07 g cm^{-3} was purchased from Sigma–Aldrich (Steinheim, Germany), and used without further purification. Stock solutions of 10.63 mM were prepared in ultrapure deionized water, stored in the amber glass bottle at 4 °C, and diluted as necessary. HPLC-grade MeOH and ACN were supplied from Merck (Darmstadt, Germany). Other reagents used in this study such as Na_2HPO_4, NaH_2PO_4, H_3PO_4, NaOH, $NaNO_3$, Na_2SO_4, NaCl, Na_2CO_3, $NaHCO_3$ and H_2O_2 were obtained from Sinopharm (Shanghai, China). Ultrapure deionized water (18 MΩ cm) was prepared in the lab using a Milli-Q water system (Millipore, USA).

2.2. Ozonation experiments

Ozonation experiments were performed in a semi-batch mode in a 1000 mL cylindrical jacketed borosilicate glass reactor. O_3 was produced from purified O_2 (99.8%) by a COM-AD-01 O_3 generator (Anseros, Germany), and was continuously bubbled into the stirred phosphate buffer solution (5 mM with different pH) through a gas-dispersion tube placed in the bottom of the reactor untill the equilibrium concentration. Afterwards, a certain amount of phenazone stock solution (diluted into the different initial phenazone concentration) was added to the reactor to stimulate reaction. Gaseous outlet from the reactor was led to an O_3 destruct device, where the remaining O_3 was destroyed by the reaction with KI. Reaction temperatures were maintained at the desired value ±0.1 °C using a circulating water bath. Stock solution of anion (SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-) and/or H_2O_2 were freshly prepared, and pre-added into the reactor before ozonation.

Investigation for transformation products from phenazone ozonation was carried out in a batch mode (Miao et al., 2010). During those experiments, an O_3 stock solution was obtained by bubbling O_3 gas through Milli-Q purified water maintained at 4 °C to maximize O_3 dissolution. The ozonation was started by injecting the O_3 stock solution through a Teflon septum into the sample with a gas-tight syringe, and shaking the reaction vessel vigorously for 60 s. Temperature of the reaction was kept at 25 ± 1 °C, and pH was adjusted by phosphate buffer. Samples for analysis were withdrawn at defined time intervals and quenched by aeration with N_2 to remove the residual O_3.

2.3. Analytical methods

The concentration of O_3 in the gas phase and solution were determined with a non-dispersive UV Photometer Anseros Ozomat GM-6000-OEM (Anseros, Germany) and indigo colorimetric method (Bader and Hoigné, 1981), respectively. Total organic carbon (TOC) analysis was carried out by a TOC-VCPH analyzer equipped with an ASI-V autosampler (Shimadzu, Japan). NO_3^- formation during ozonation was determined using a Metrohm ion chromatograph (883 Compact IC Pro, Switzerland) equipped with a Metrosep A Supp 5 (250 × 4.0 mm^2) analytical column. The eluent used was 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ at the flow rate of 0.7 mL min^{-1}, and the sample loop volume was 20 μL (Ismail et al., 2013). Phenazone analysis was performed by HPLC (Agilent 1200, USA) equipped with a Kromasil C_{18} (250 × 4.6 mm^2, I.D. 5 μm) column. The mobile phase was a mixture of ACN and water (75%: 25%) at an isocratic flow rate of 1.0 mL min^{-1} at room temperature. Injections were performed with a 20 μL loop and wavelength of the UV absorbance detector was 270 nm (Tan et al., 2013a).

Identification of phenazone transformation products was carried out by ultra performance liquid chromatography in combination with time-of-flight mass spectrometry (UPLC-Q-TOF-MS) (Rodil et al., 2012). UPLC was performed with Waters Acquity UPLC system (Milford, MA, USA) equipped with a binary solvent-delivery system and an autosampler. Chromatography was performed on a Waters Acquity C_{18} column (2.1 × 50 mm^2, 1.7 μm particle). The mobile phase was a gradient prepared from ACN (component A) and 0.1% formic acid aqueous solution (component B). Elution started with 5% A for 0.1 min then the proportion of A was increased linearly to 50% in 7.9 min, then to 100% in 2 min, and then returned to initial conditions within 0.1 min, and kept isocratic for 1 min. The flow rate was 0.3 mL min^{-1}, and the injection volume was 10 μL. Mass spectrometry was performed on Waters Synapt Q-TOF system (Milford, MA, USA) fitted with an electrospray ionization (ESI) source operating in positive ionization (PI) mode, with the optimum conditions set as follows: capillary voltage to 3.5 kV, cone voltage to 30 V, source temperature to 100 °C, and desolvation temperature to