

Sulfamethoxazole and sulfadiazine treatment by the hot persulfate process

Minghua Nie¹⁾ and *Wenbo Dong²⁾

^{1), 2)} *Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention,
Department of Environmental Science and Engineering, Fudan University, 220 Handan
Road, Shanghai 200433, China*

²⁾ wbdong@fudan.edu.cn

ABSTRACT

The feasibility of using thermally activated persulfate (TAP) to degrade sulfamethoxazole (SMX) and sulfadiazine (SD) in aqueous solution were evaluated. Results showed that both compounds degradation followed a pseudo-first-order model under all conditions tested and the observed rate constants well fitted the Arrhenius equation. These two contaminants degradation rate constants (k_{obs}) increased with increased temperature and sodium persulfate (SPS) dosage. It clearly shows alkaline conditions is more favorable than neutral and acidic conditions for SMX degradation in TAP process. Unlike SMX, the degradation rate of SDZ in TAP system was highest at pH 3 and decreased with an increase solution pH.

1. INTRODUCTION

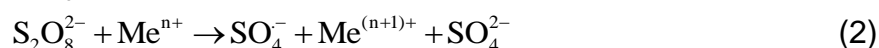
Sulfonamides (SAs) such as sulfamethoxazole (SMX) and sulfadiazine (SDZ) have been extensively used throughout the world to treat gram-positive and gram-negative microorganisms-caused diseases include urinary-tract infections, meningococcal meningitis and pneumocystis pneumonia (Sarmah 2006). Previous studies have found these two compounds in the aquatic environment may lead to the spread of antibiotic-resistant bacteria, which may pose a serious health threat to humans and ecological receptors (Yan 2013). Unfortunately, SMX and SD are refractory to conventional treatments employed in the wastewater treatment plants (WWTPs), thus trace SMX and SD have often been found in effluents, as well as in natural surface waters (Zheng 2011). Therefore, the development of effect treatment for eliminating SMX and SD in water becomes highly necessary.

In the last decades, advanced oxidation processes (AOPs), such as ozonation, Fenton process, sonification, ionizing radiation, photolysis and heterogeneous photocatalysis, have been applied for the removal of SMX and SD and demonstrated to be highly effective. Recently, persulfate ($S_2O_8^{2-}$, PS) has attracted increasing attention as alternative oxidant in the oxidation of organic pollutants. There are numerous advantages in the use of PS: low cost, high redox potential ($E_0=2.01$ V), high solubility

¹⁾ Graduate Student

²⁾ Professor

in water, non-selectively reactive and high stability at room temperature. It can be activated by UV light, heat, or transition metal ions (Eq (1) and (2)) to produce sulfate radicals ($\text{SO}_4^{\cdot-}$), which has been known as a strong oxidant with a redox potential of 2.60 V, similar to that of hydroxyl radical ($\cdot\text{OH}$, 2.7V). In addition, $\text{SO}_4^{\cdot-}$ radicals have a much longer half-life and more selectivity for the oxidation of target organic pollutants compared to $\cdot\text{OH}$ radicals (Jiang 2013).



Among the three activation methods, thermally activated PS (TAP) is considered as a clean source of $\text{SO}_4^{\cdot-}$ radicals have been proved efficient for the oxidation a wide variety of organic pollutants. Previously, the degradation of SMX using PS has been investigated using ferrous iron activation and zero-valent iron activation in aqueous solutions, and zero-valent iron activation was found to be more efficient than ferrous iron activation process (Ji 2014; Ghauch 2013). However, the oxidation of SMX contaminated water by thermally activated PS has not been explored. Moreover, to the best of our knowledge, there has not been any study on $\text{SO}_4^{\cdot-}$ oxidation of SD in water.

This study made the first attempt to examine the degradation of SMX and SD by TAP process. The performance of the TAP process was evaluated through the examination of some critical parameters, including temperature, PS concentration, solution pH.

2. Materials and methods

2.1 Materials

SMX ($\geq 99.5\%$) and SD ($\geq 99.5\%$) were purchased from J&K. Methanol (MeOH, HPLC grade; $\geq 99.9\%$) was obtained from CNW Technologies GmbH, Germany. The other reagents including ethanol (EtOH; $\geq 99.9\%$), sodium phosphate (Na_2HPO_4 ; $\geq 99.0\%$), monobasic sodium phosphate (NaH_2PO_4 , $\geq 99.0\%$), sodium hydroxide (NaOH; $\geq 99.8\%$), sulfuric acid (H_2SO_4 ; $\geq 98.0\%$) were purchased from China National Medicines Corporation Ltd. (Beijing, China). All chemicals were at least analytical grade. All the solutions were prepared using deionized water.

2.2 Experimental procedure

Batch experiments were carried out in a set of 150 mL-capacity glass water-jacketed beakers containing 100 mL aqueous solution. The temperature was kept constant at a desirable level during all experiments by circulating the hot water through the jacket around the reactors using a thermostat circulating water bath. A magnetic stirrer located at the base of the reactor ensured a complete solution mixing state. The SMX or SDZ concentration was fixed at 0.05 mM. The oxidation reaction was initiated by adding the corresponding volumes of 80 mM SPS stock solution and other chemicals were added. The initial pH in all experiments was unadjusted except in the tests for investigating the effect of pH. When investigating the effect of pH, the reaction pH was

adjusted to desirable values by adding 0.2 M Na_2HPO_4 , 0.2 M NaH_2PO_4 , 0.2 M NaOH or 0.2 M H_2SO_4 as needed.

At each designated time interval, 1 mL of aqueous sample was collected and stored in a 1.5 mL sample vial, then chilled at 4 °C in cold water for approximately 10 min to quench the oxidation reaction. All batch experiments were performed in triplicate at least with standard deviation < 5% and mean values reported.

2.3 Analytical methods

Concentrations of SMX and SDZ were analyzed using a high-performance liquid chromatography (HPLC) (Ultimate 3000, Dionex, USA) equipped with an XDB-C18 analytical HPLC 5 μm (4.6 mm \times 150 mm) reversed-phase column and a variable UV-vis wavelength detector. SMX analysis was carried out with a 60: 40 MeOH: acetic acid solution (pH 3.06) mobile phase at a flow rate of 0.8 mL/min with a detection wavelength of 265 nm. Analysis for SDZ used a 70:30 MeOH: acetic acid solution (pH 3.06) mobile phase at a flow rate of 0.8 mL/min with a detection wavelength of 275 nm. Solution pH was measured using a pH meter (INESA Scientific Instrument Co., Ltd, China).

3. Results and discussion

3.1 Effect of temperature

There were almost no observable SMX and SDZ removal when heating was applied in the absence of SPS, nor were there SMX and SDZ removal after addition of SPS without heating. In contrast, both SMX and SDZ can be degraded with TAP oxidation and well follow an apparent pseudo-first-order kinetics pattern ($R^2 > 0.95$) (Fig. 1). The degradation efficiencies of SMX and SDZ were approximately only 15% and 5% at 40°C over 80 min; as the temperature increases to 90 °C, almost complete SMX and SDZ removal are observed over 30min.

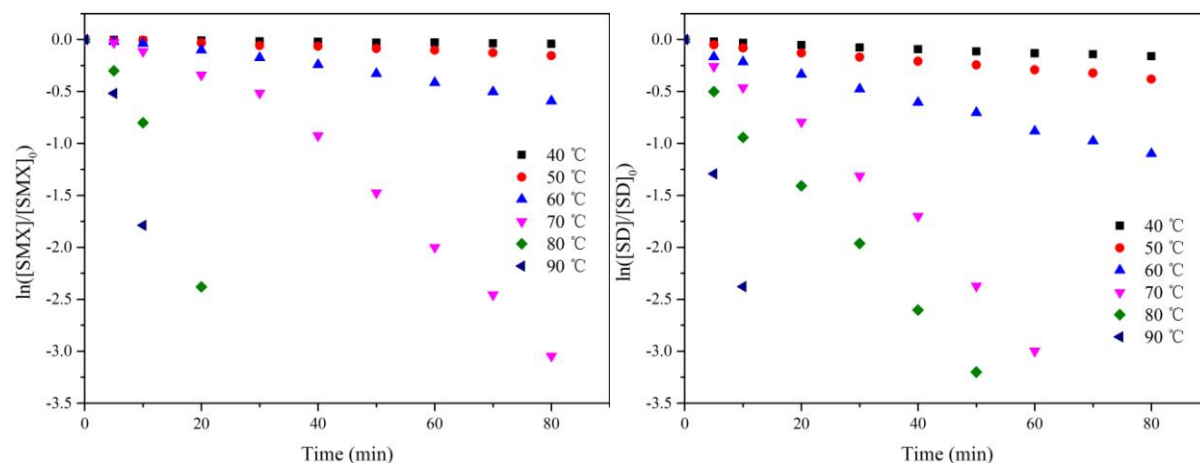


Fig. 1 SMX and SD degradation using TAP oxidation under different temperatures.

3.2 Effect of SPS dosage

The effect of the SPS dosage on SMX and SDZ degradation was investigated within the SPS dosage ranges of 0.05-2 mM at 70 °C. As exhibited in Fig. 2, for any

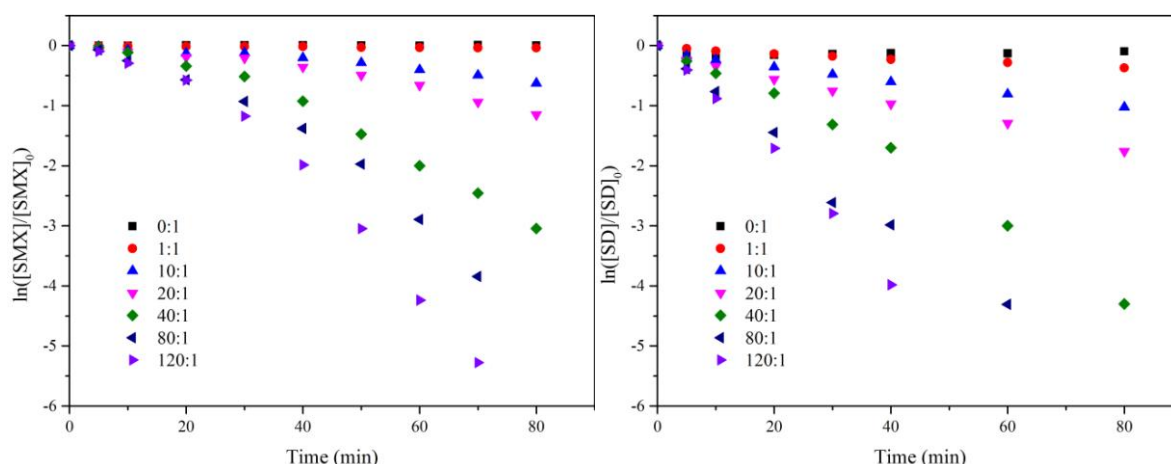


Fig. 2 SMX and SD degradation using TAP oxidation under different SPS dosage.

particular SPS dosage, the degradation rates of both SAs abide by pseudo-first-order kinetics. Moreover, the k_{obs} values was positively proportional to SPS dosage in this study. Similar result was observed by Nie (2014), who reported that the degradation rate of chloramphenicol was exhibit a linear trend as a function of SPS dosage.

3.3 Effect of solution pH

The effect of solution pH (3-11) on the SMX and SDZ degradation by TAP oxidation is shown in Fig. 3. The results indicated that the constant rate of both SAs degradation was pH-dependent. It clearly shows alkaline conditions is more favorable than neutral and acidic conditions for SMX degradation in TAP process. The rate constants of SMX degradation were in the following order: pH 11>pH 9> pH 7>pH 3> pH5. As the pH decreases from 11 to 5, the SMX degradation rate constant accordingly decreases. This result was in accordance with the findings of Tan that the observed rate constant decreased through pH 11 to pH 9 during TAP oxidation of antipyrine (Tan 2013). Similarly, Ghauch et al. investigated the effect of pH on TAP oxidation of ibuprofen and found that the reaction rate increased from pH 7 to pH 9 (Ghauch 2012). However, when the pH down to 3, the degradation rate of SMX achieves a certain degree of increase.

Unlike SMX, the degradation rate of SDZ in TAP system was highest at pH 3 and decreased with an increase solution pH (Fig. 3), indicating that acidic conditions are propitious to SDZ oxidation. The results were in agreement with the rate constants of carbamazepine and antipyrine oxidation by TAP process which decreased with an increasing pH 3 to pH 9 (Tan 2013; Deng 2013).

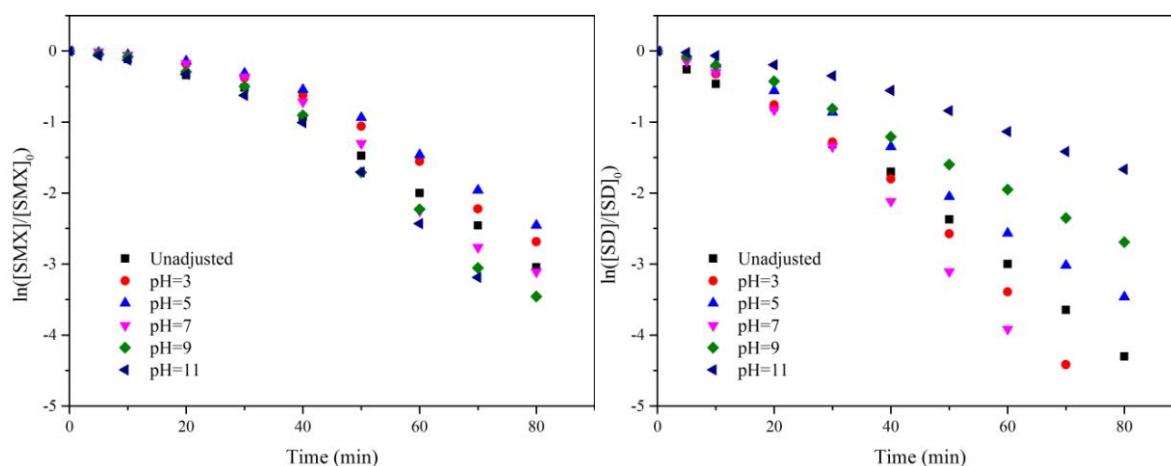


Fig. 3 SMX and SD degradation using TAP oxidation under different solution pH.

4. CONCLUSIONS

The kinetics and mechanism of SMX and SD degradation using TAP oxidation were investigated in the present work. The reaction kinetics was attributed pseudo-first order rate with respect to SMX and SD. Both two compounds decomposition were significantly influenced by operating temperature, oxidant concentration, solution pH. These two compounds degradation rate increased with increased temperature and SPS dosage. It clearly shows alkaline conditions is more favorable than neutral and acidic conditions for SMX degradation in TAP process. Unlike SMX, the degradation rate of SDZ in TAP system was highest at pH 3 and decreased with an increase solution pH.

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