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Degradation Characteristics of Sulfamethoxypyridazine in Water by Ozonation and Photocatalysis

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Abstract

Pharmaceuticals and personal care products (PPCPs) have emerged as a major class of contaminants, given their widespread usage and known biological effects. Sulphonamides are synthetic antibacterial agents widely used in veterinary practice for the treatment of infections and to promote the growth of food-producing animals. Traditional sewage treatment procedures are unable to get rid of these compounds effectively. Advanced oxidation processes (AOPs) are a promising technology for treating wastewaters containing sulfamethoxypyridazine pharmaceuticals via O₃ and UV/TiO₂ process. This study performs batch experiments to determine the effects of operating parameters on the degradation efficiencies of sulfamethoxypyridazine. The degradation was studied by monitoring the intermediates employing high performance liquid chromatography (HPLC) separation coupled to an atmospheric pressure ionization mass spectrometry (API-MS) system operating under selected ion monitoring (SIM). Results show that complete removal of all sulfamethoxypyridazine was achieved within 80 min of ozonation at the concentration of O₃ (3 ppm) at different pH runs. The ozonation of sulfamethoxypyridazine demonstrated the best degradation efficiency for runs at pH 8, followed by runs at pH 6 and pH 11. The ozonation imposed sulfamethoxypyridazine with a time dependence that appeared to follow pseudo first-order kinetics. The original concentration of sulfamethoxypyridazine almost completely degraded within 7 hr in UV/TiO₂ at pH 6 runs. The reaction rates for the decomposition of sulfamethoxypyridazine in water are higher at pH 6 run than for runs at pH 3 and pH 11. Three organic intermediates appeared during the photocatalytic degradation of sulfamethoxypyridazine.

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Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).**Keywords:** Pharmaceuticals, Sulfamethoxypyridazine, Advanced Oxidation Processes, Ozonation, TiO₂^{*} Corresponding author. Tel.:E-mail address: andylo@hk.edu.tw

1. Introduction

Sulfa pharmaceuticals are synthetic antibacterial agents widely used in veterinary practice for the treatment of infections and promoting the growth of food-producing animals. However, the persistence of these substances in food is of great concern, particularly because of their potential carcinogenic characteristics [1]. For example, the improper use of these sulfa pharmaceuticals in cows has caused the presence of sulfa pharmaceuticals in milk. Therefore, monitoring these residues in slaughtered animals and in products destined for human consumption [2] has become one of the most essential duties for public health agencies [3]. The animal waste from intensive farming that is often collected for field fertilization may contain drug residues; thereby introducing these chemicals to agricultural soils. Traditional sewage treatment procedures are unable to get rid of these compounds effectively. Advanced oxidation processes (AOPs) involve the generation of hydroxyl radicals and other strong oxidant species that are able to degrade compounds characterized by high chemical stability [4-6]. The objective of this study is to evaluate the removal efficiencies of PPCPs via O₃ and UV/TiO₂ processes. To probe the environmental transformation characteristic and the general degradation law of these sulfa pharmaceuticals, the experiments in this study conducted and compared ozonation and photocatalytic degradation kinetics using sulfamethoxypyridazine (C₁₁H₁₂N₄SO₃) as a model compound.

2. Materials and Methods

2.1 Ozonation experiments

Ozonation runs were performed in a 1-L glass trap flask. Ozone was supplied by an ozonator (OW-K1/A/O) at 5 % ozone in the gas phase at a gas flow of up to 1 Lmin⁻¹. The ozone concentration was determined by an iodide method (Method 2350E) [7]. Experiments were performed at pH 6, 8, and 11 under various concentrations of ozone. The concentration of ozone supplied ranged from 1 and 3 ppm, respectively. The initial concentration of sulfamethoxypyridazine solution was 20 ppm. Experiments were conducted at room temperature (25 °C).

2.2 Photocatalytic experiments

Photocatalytic experiments were conducted in a hollow photoreactor with a nitrogen cooling system. The photoreactor measured 18×18×21 inches (length×width×height) and the center of the photoreactor was 10×15 inches (diameter×depth). The photoreactor was equipped with a UV lamp (RPR-3650, 8W×4, 365 nm). Batch experiments were performed at different pH runs (pH 3, 6, and 11, respectively). The required amount of TiO₂ (P-25, Degussa) powder (2 gL⁻¹) was added to an initial sulfamethoxypyridazine (99 %, Aldrich, USA) concentration of 10 ppm and then transferred to the photoreactor for an equilibration period of 30 min under darkness. The UV lamp was turned on immediately after the stock solutions of sulfamethoxypyridazine were added. Aliquots were extracted from the solution for analysis at various times after the catalysts had been removed by centrifugation at 8000 rpmmin⁻¹ for 20 min.

2.3 Analytical procedures

Sulfamethoxypyridazine was quantified using high-performance liquid chromatography (HPLC) with an Agilent HC-C18 column (5μm, 25 cm × 4.6 mm) system. The mobile phase was 80 % of acetonitrile (99.5 %, Merck, Germany). The elution was delivered at a rate of 1 mLmin⁻¹ and the wavelength for

detection was 254 nm. This method allows for the determination of the intermediates of sulfamethoxy pyridazine by HPLC separation coupled to an atmospheric pressure ionization mass spectrometry (API-MS) system (Agilent 6120) operating under selected ion monitoring (SIM).

3. Results and discussion

3.1 Degradation of sulfamethoxy pyridazine by ozone

The concentration vs. time profiles of the sulfamethoxy pyridazine solution are individually subjected to ozonation (1 and 3 ppm, respectively) at different pH runs (Fig. 1). These results indicate that the normalized concentration (C/C_0) of sulfamethoxy pyridazine decreased as the ozonation time increased. The original concentration of sulfamethoxy pyridazine almost degraded within 90 min and 80 min at ozone concentrations of 1 and 3 ppm, respectively, at different pH runs. Accordingly, the ozonation imposed sulfamethoxy pyridazine with a time dependence that appeared to follow pseudo first-order kinetics [8]. The rate constants were calculated as 0.02, 0.02, and 0.01 min^{-1} at pH 6, 8, and 11, respectively, at an ozone concentration of 1 ppm. The rate constants were calculated as 0.02, 0.06, and 0.04 min^{-1} at pH 6, 8, and 11, respectively, at an ozone concentration of 3 ppm. These results indicate that the reaction rates for the ozonation of sulfamethoxy pyridazine in water are higher under the concentration of ozone 3 ppm. The ozonation of sulfamethoxy pyridazine demonstrated better degradation efficiency for runs at pH 8 than for runs at pH 6 and pH 11, respectively.

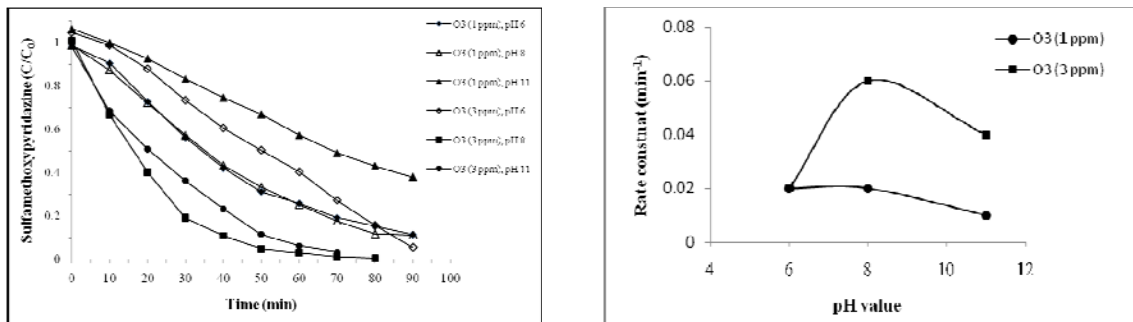


Fig. 1. Effect of pH on sulfamethoxy pyridazine ozonation : effect of varying pH (left); rate constants (right)

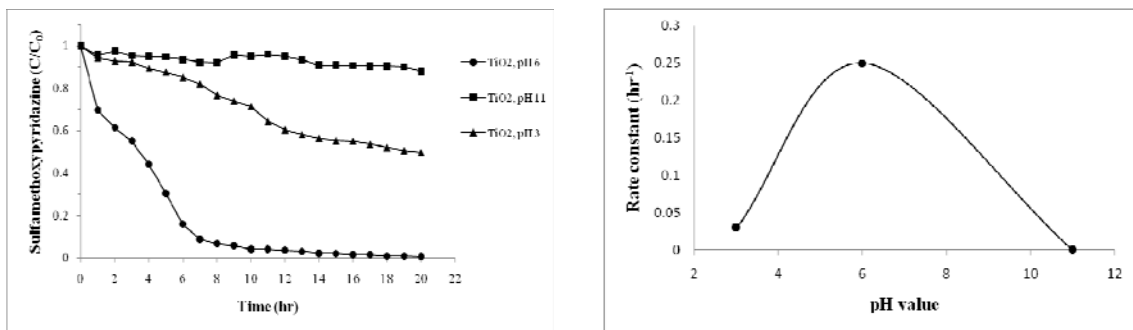
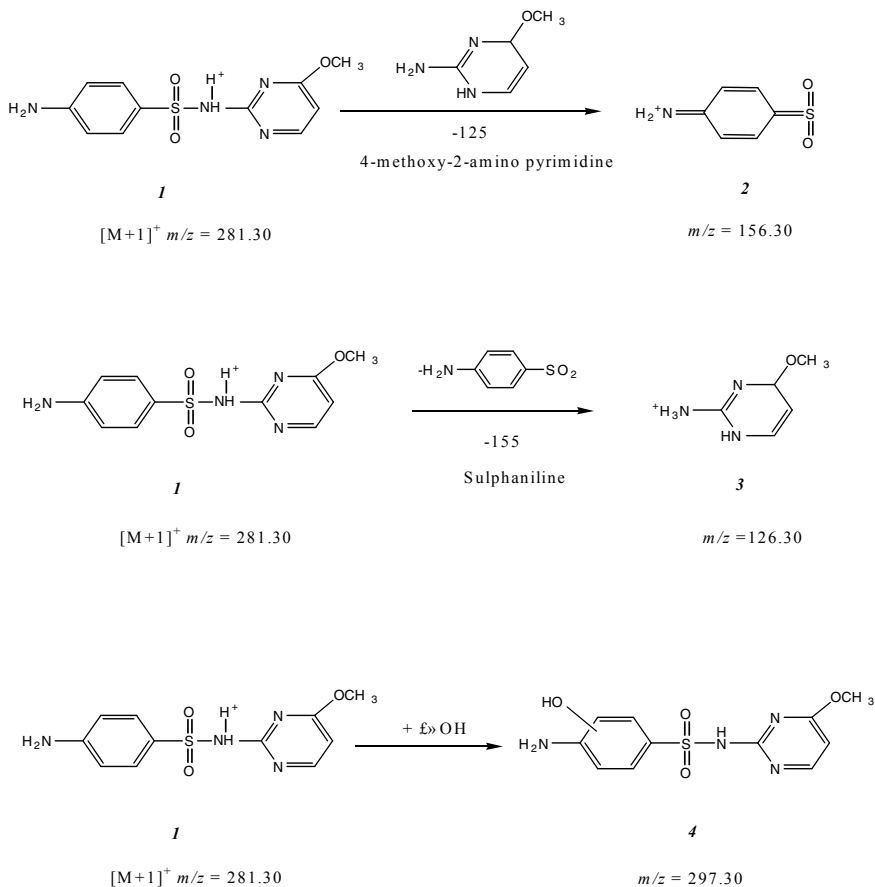


Fig. 2. Effect of pH on sulfamethoxy pyridazine photocatalytic degradation: effect of varying pH (left); rate constants (right)

3.2 Degradation of sulfamethoxy pyridazine by UV/TiO₂ process

Figure 2 shows the degradation efficiency of sulfamethoxy pyridazine in UV/TiO₂ for pH 3, pH 6 and pH 11 runs. These results indicate that the normalized concentration (C/C_0) of sulfamethoxy pyridazine decreased as the photocatalytic time increased at pH 3 and pH 6, respectively. The normalized concentration of sulfamethoxy pyridazine appeared constant as the photocatalytic time increased at pH 11. The original concentration of sulfamethoxy pyridazine almost completely degraded within 7 hr of irradiation at pH 6. While the catalysts yielded a sulfamethoxy pyridazine time dependence that appeared to follow pseudo first-order kinetics, these results indicate that the reaction rates for the decomposition of sulfamethoxy pyridazine in water are higher ($k = 2.5 \times 10^{-1} \text{ hr}^{-1}$) at pH 6 run than for runs at pH 3 ($k = 0 \text{ hr}^{-1}$) and pH 11 ($k = 3 \times 10^{-2} \text{ hr}^{-1}$), respectively. The high rate constants at low pH (pH 6) for sulfamethoxy pyridazine are because it is difficult to protonate in weak acidic solution. These neutral structures of sulfamethoxy pyridazine can be adsorbed onto the positively charged TiO₂ surface below the zero point. On the other hand, with a further increase in the pH value, sulfamethoxy pyridazine may lose a proton and exist in anionic form. Hence, the negative sulfa pharmaceutical molecule cannot be easily adsorbed onto the surface of TiO₂ surface with the same negative charges (pH>6.3).

Scheme 1



3.3. Identification of intermediates and degradation pathway

The API with electrospray ionization (EI) plus chemical ionization (CI) mass spectrum of sulfamethoxy pyridazine is showed the molecular ion M^+ (m/z 280.30) and protonated sulfamethoxy pyridazine (m/z 281.30). The fragmentation of $[M+H]^+$ ion of sulphonamides created daughter ion spectra characterized by common ions at m/z 92, 108, and 156 and ions at m/z $[M+H-155]^+$ derived from the amine substituent [1, 9]. Three organic intermediates appeared (Scheme 1) during the photocatalytic degradation of sulfamethoxy pyridazine. The degradation of sulfamethoxy pyridazine and these intermediates was almost complete within 7 hr. Intermediate 2 was identified as sulphanylne with $m/z = 156.30$. Intermediate 3 was identified as 4-methoxy-2-amino pyrimidine with $m/z = 126.30$ for MH^+ . Intermediate 4 was identified as hydroxylated sulfamethoxy pyridazine with $m/z = 297.30$ for MH^+ .

4. Conclusions

This study investigates the ozonation and photocatalytic degradation kinetic of sulfamethoxy pyridazine in aqueous solution in detail. Results show that ozonation resulted in almost completely degraded sulfamethoxy pyridazine within 90 min at a concentration of 20 mgL^{-1} . Ozonation demonstrates superior removal efficiency of sulfamethoxy pyridazine at an ozone concentration of 3 ppm at pH 8. Sulfamethoxy pyridazine can also be degraded with removal efficiencies of 100% within 20 hr by a TiO_2/UV process at pH 6. The photocatalytic degradation of sulfamethoxy pyridazine produced three intermediates, identified as sulphanylne, 4-methoxy-2-amino pyrimidine, and hydroxylated sulfamethoxy pyridazine.

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