

Photocatalytic activity of sulfonamide antibiotic in aqueous suspension of TiO₂-P25

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Abstract—This study investigated the photo-degradation mechanisms of sulfamethazine (SMT) by commercial titanium dioxides (TiO₂-P25). The results showed that the photo-degradation of SMT occurred under the irradiation of ultraviolet-C light (UVC: 254 nm) with or without TiO₂ and the presence of TiO₂ enhanced the photo-degradation rate of SMT. Photocatalysis degradation rate was described by pseudo-first order kinetics. The degradation rate decreased with increasing the initial concentration. The presences of radical scavengers (isopropanol and NaI) inhibited photocatalytic degradation of SMT, indicating the involvement of holes on TiO₂ and OH radicals in the photo-degradation of SMT.

Keywords: photocatalysis; TiO₂; Sulfamethazine

I. INTRODUCTION

The presence of antibiotics in aquatic media has emerged in the last decade as a new environmental risk [1]. Sulfonamides (SMTs) are important bacteriostatic agents, commonly used in human and veterinary medicines [2]. SMTs are released into the environment via industrial effluents (i.e. drugs industrial residues), and household and hospital wastewaters [1, 3]. Although the concentration of SMTs is usually low, its long life-time in the environment can result in its accumulation in food chains [2].

In order to eliminate this substance in wastewaters, conventional secondary wastewater treatment processes (WWTPs) appear to be highly variable [4]. SMTs appear to be only partially removed by conventional WWTPs, due to moderate sorption to sludge and limited biodegradability [4].

Heterogeneous photocatalysis technique using a semiconductor as catalyst has been applied to eliminate many types of organic contaminations in water. Among various semiconductor materials such as oxides and sulfides, a lot of attention has been given to TiO₂ because it is cost-effective and has a high photocatalysis activity and resistance to photo-corrosion, (biological immunity or biologically inert) [3]. This photo-catalysis process of

TiO₂ involves the generation of electron-hole pairs, which control the occurrence of redox reactions of species adsorbed on the photocatalyst surface [5].

This study is aimed at understanding the photo-degradation efficiency and mechanism of sulfamethazine (C₁₂H₁₄N₄O₂S, pKa=7.4) on TiO₂. The effects of pH, photocatalyst concentration, initial concentration of sulfamethazine and presence of radical scavenger on the photo-degradation of SMT were also investigated.

II. MATERIALS AND METHODS

Sulfamethazine (C₁₂H₁₄N₄O₂S, ≥ 99%, SMT) were obtained from Sigma-Aldrich. An aqueous stock solution (100 mg L⁻¹) was prepared and kept at 4°C in the dark. Commercial TiO₂ Degussa P25 (80% anatase and 20% rutile) were used as the photocatalyst. Experiments were carried out under UV-C irradiation (254 nm) in a confined bin. A quartz beaker with 500 ml aqueous SMT solution was placed in the reactor. The pH of solution was adjusted by 0.1 M HCl and NaOH. In photolytic degradation experiments, no TiO₂-P25 was added to the beaker containing SMT solution. In the experiments of photo-catalytic degradation, SMT solutions with concentrations ranging from 9 to 45 mg L⁻¹ were reacted with 0.5 g L⁻¹ of TiO₂-P25. In order to confirm the removal of SMT is due to photolysis or photocatalysis, UV irradiation was initiated after 1 h of reaction in the dark, at which adsorption equilibrium was achieved. Ten ml suspensions were withdrawn at fixed time intervals [5] and were passed through a 0.2-μm cellulose acetate filter (Advantec) to collect the filtrates. The filtrate were then mixed with a pH 11 buffer solution which consisted of 0.5 M Na₂HPO₄ (100 ml) and 0.1 M NaOH (8.2 ml). The residual concentration of SMT was determined with UV-vis spectrophotometer at 268 nm. The kinetic data were fit using pseudo-first order equation. The initial degradation rate was determined using the kinetic data obtained from the first 20 min to exclude the contribution

from intermediates generated from the photo-degradation reaction [3].

To investigate the mechanism of photocatalysis, isopropanol and sodium iodide were added to the reaction mixture to scavenge hydroxyl radicals, superoxide radicals, and hole, respectively.

III. RESULTS AND DISCUSSION

At first, experiments concerning the photolytic degradation of 9 mg L^{-1} SMT was performed under UV-C irradiation for 4 hr and the result are show in Figure 1. With increasing pH, the degradation rate of SMT increased. It suggests the degradation of sulfamethazine consist with other causes such as the species of sulfamethazine[6].

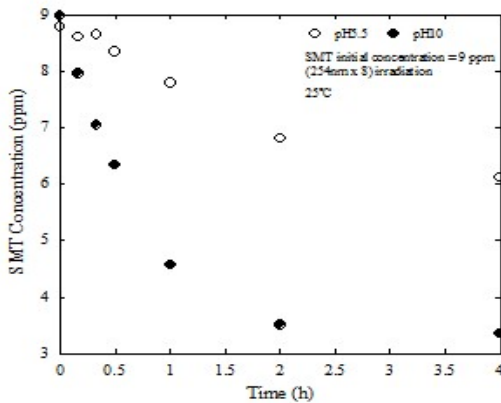


Fig. 1. Photolysis of 9 mg L^{-1} SMT as a function of irradiation time at pH 10 and pH 5.5

Figure 2 shows the blank experiment, in which SMT solution was stirred in dark condition and no destruction of SMT occurred. When $\text{TiO}_2\text{-P25}$ was added to the SMT solution at the same experimental condition, the concentration of SMT slightly decreased (<5%), attributed to the adsorption of SMT on TiO_2 . At pH 5.5, both SMT and TiO_2 have positive charges so the electrostatic repulsion between the adsorbate and adsorbent resulted in a low adsorption of SMT on TiO_2 .

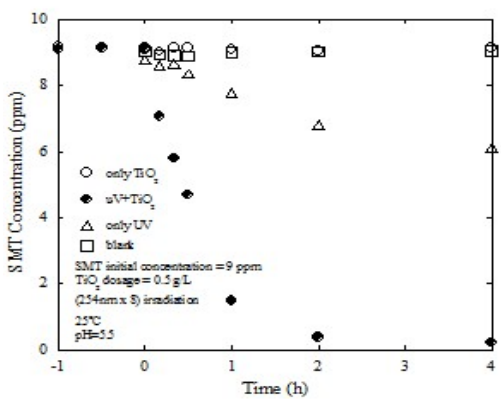


Fig. 2. Photocatalysis of 9 mg L^{-1} SMT as a function of irradiation time at pH5.5

The effect of initial SMT concentration on the photocatalytic decomposition rate of SMT could be described to be pseudo first order kinetics and the k_s value was calculated base on the pseudo first order equation. Figure 3 shows that the rate of photocatalytic degradation decreased with increasing the initial concentration of SMT. This result may be attributed to the light absorption capacity of titanium dioxide, because more SMT molecules in the solution will compete with TiO_2 for the UV light. The rate parameters of photocatalytic list on table I.

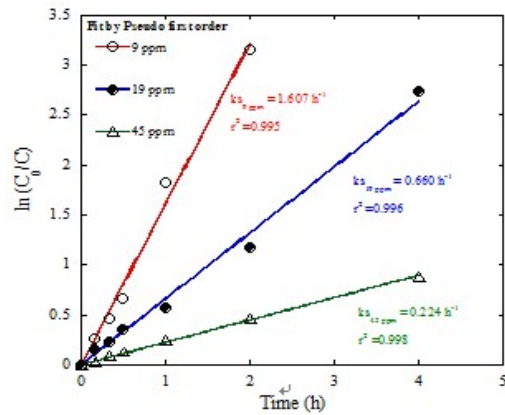


Fig. 3. Plot $\ln(C_0/C)$ v.s. time at different SMT concentration for constant concentration of $\text{TiO}_2\text{-P25}$ at 0.5 g L^{-1} .

Radical scavengers was used to assess the photocatalytic reaction mechanism of SMT because this approach can alter the kinetic profile of the reaction, and provide information about the participation of different radicals[7]. Isopropanol has been proposed to discern the role of hydroxyl radical in oxidation mechanism[8]. The formation of iodide from a solution containing iodide anions and a photocatalyst under irradiation ($h^+ + \text{I}^- \rightarrow \text{I}_2$) can be used to identify the involvement of holes on TiO_2 in the oxidation of organic substrates[9]. The results are show in Figure 4. When the isopropanol or sodium iodide was added in the SMT solution, photocatalytic activity was decreased. It is suggesting the participation of hydroxyl radical and electron hole in the reaction mechanism.

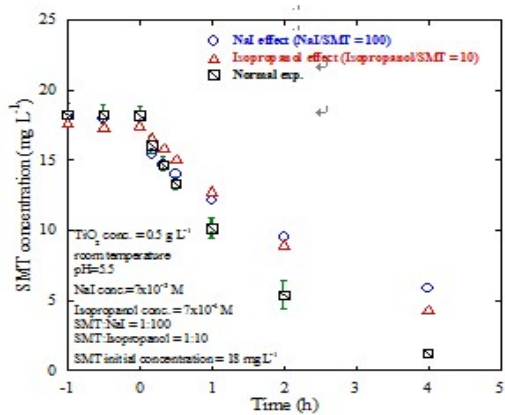


Fig. 4. Photocatalysis of 20 mg L⁻¹ SMT as a function of irradiation time at pH5.5

TABLE I. THE RATE OF PHOTOCATALYSIS IN VARIOUS INITIAL CONCENTRATION OF SULFAMETHAZINE.

concentration (ppm)	Rate of photocatalysis (hr ⁻¹)	r ²
9	1.61	0.995
19	0.66	0.996
45	0.22	0.998

IV. CONCLUSIONS

Base on the experimental results, the photolytic activity degradation of SMT under UV-C irradiation was enhanced with increasing pH the rate of photocatalysis has a negative effect. Addition of radical scavenger revealed photocatalytic mechanisms of sulfamethazine on TiO₂ involving holes and OH radicals.

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