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Aqueous Photodegradation of Selected Antibiotics under Different Conditions

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***Abstract*—Different aqueous photodegradation behaviors of sulfamethoxazole, trimethoprim and sulfapyridine were investigated under different conditions in this study. Comparison of degradation rates of selected pharmaceuticals among different aqueous media under high pressure mercury lamp, natural light and UV lamp were shown. Results showed that light source, pH, temperature, time and different aqueous solutions were important factors for photodegradation of these antibiotics and also demonstrated photodegradation was an important environmental fate of these antibiotics.**

Keywords- high pressure mercury lamp; natural light; UV; pH; temperature

I. INTRODUCTION

Sulfamethoxazole (SMX), trimethoprim (TRM), and sulfapyridine (SPY) are widely used in humans and animals as common antibiotics for long years. So far, these drug residues have been detected in wastewater treatment plant, biosolids, soil, and etc [1-4]. Recent research showed that the amount of different drug residues discharged to environment is increasing year by year [5, 6]. It is not only threatening to ecological system, such cause occurrences of some drug-resistant pathogens and toxic to some aquatic species, but also harmful for human health by food chain [7-9].

Photodegradation is one of the major transformation processes affecting the fate of pharmaceuticals in the environment. Many reports have showed that many pharmaceuticals can be degraded under sunlight, UV, ozone, and other advanced oxidation conditions [10-12]. In this study, the photolysis behavior of the selected antibiotics under different conditions was investigated.

II. MATERIALS AND METHODS

A. Chemicals

The pharmaceuticals used in the study (purchased from Sigma) are SMX (pKa 1.7/5.6), TRM (pka 1.3/7.4) and SPY (pKa 2.3/8.4). All compounds were of at least analytical grade.

B. Photolysis Experiments under High Mercury Lamp, Natural Light and UV lamp

Under temperature control chamber (22 ± 3 ºC), all the glass tubes were exposed to high pressure mercury lamp (MVR400/U). The illumination lasted for 42 d. Samples were collected at 0, 2,7,14,21,28,35 and 42 d respectively.

Under direct natural light, all the glass tubes were exposed to natural light on daytime and night-time. It lasted for 72h outside the faculty of land and water, South Australia (approximately latitude 34.9 s.).HOBO Pendant logger was used to keep records on temperature and light intensity simultaneously. Unwrapped samples were collected at 0, 2, 4, 6, 8, 22, 24, 26, 28, 30, 32, 48, 50, 52, 54, 56 and 72 h. Wrapped samples (control samples) were collected at 0, 2, 8, 22, 32, 48, 56 and 72h, respectively.

Under UV-lamp (Philips, 30W) illumination, different solutions of selected pharmaceuticals were set at 2 mg/L in each 200-mL beaker. The solutions were humic acid (HA, 10 mg/L, pH=6), buffer (pH=9), Milli Q water (MQ, pH=7), Fe^{3+} (0.0001M, pH=4), Fe^{2+} (0.0001M, pH=5).It lasted for 8h and evaporation of solution was neglectable. The temperature was at 22 ± 3 ºC .Samples were collected every hour respectively.

For photodegradation under high mercury lamp and natural light, initial concentration of each pharmaceutical in solution was set at 2 mg/L in a 30-mL glass tube and initial pH values of solution were adjusted to 4, 7, and 9 by HCl, NaOH and NaCl. Control samples were wrapped with aluminium foil. For photodegradation under UV lamp, control samples were tested just in the beginning and the end in the experimental hours.

C. Chemicals Analysis

The concentration of SMX, TRM and SPY was determined by HPLC-UV Detector (Agilent Technologies, series 1100) equipped with a C-18 column (4.6 mm×250 mm, 5 μm，10 mm, Alltech). The detection wavelength was 280 nm and the oven temperature was set at 28 ◦C. The mobile phases used were (A) 0.3% acetic acid in ultra-pure water and (B) acetonitrile. A gradient chromatographic elution was obtained by initially running 80% A, descended to 40% in 12 min followed by increment of A phase to 80% in 2 min. Then 5 min was held for equilibrium. The run was completed in 19 min. The flow was set at 1mL/min and injection volume was 20μL.

III. RESULTS AND DISCUSSIONS

A. *Temperature control chamber*

As can be seen from Fig.1, different degradation rates were displayed for SMX and SPY, and they were significantly affected by pH. Degradation rate of SMX was a little faster on acid or alkaline condition, and it went up close to 30% at pH 4, while degradation rate of SPY was faster under neutral or alkaline condition, and it went up close to 35% at pH 7 in 42d. Degradation data of SMX and SPY were well fitted to first-order kinetics. However, there was nearly no degradation for TRM at selected pH in 42d.It was consistent with the previous report that the time for 10% trimethoprim degradation at 25 °C would be 885 days [13].

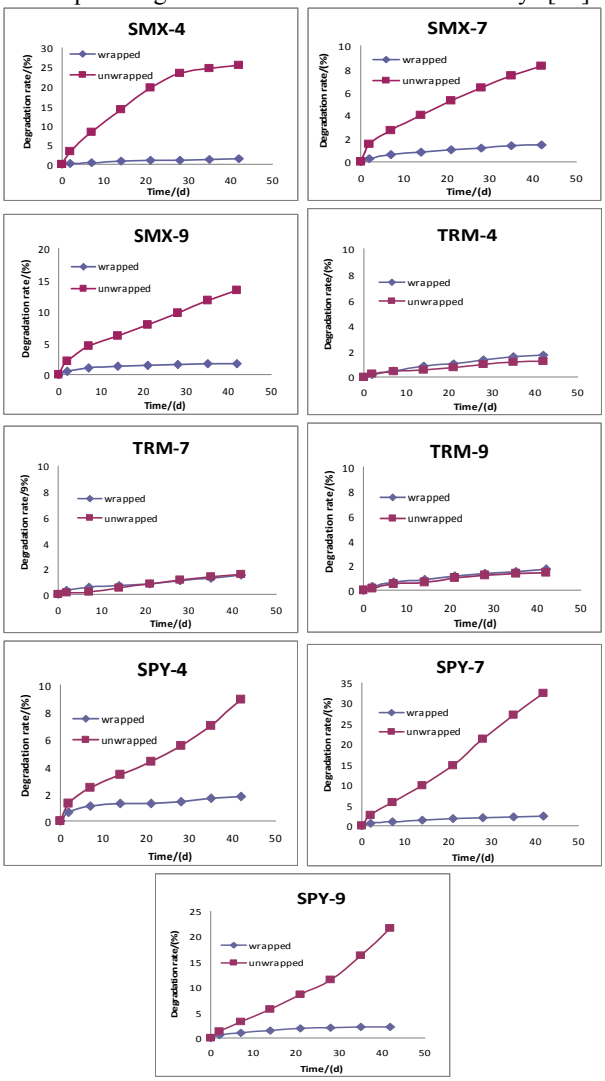
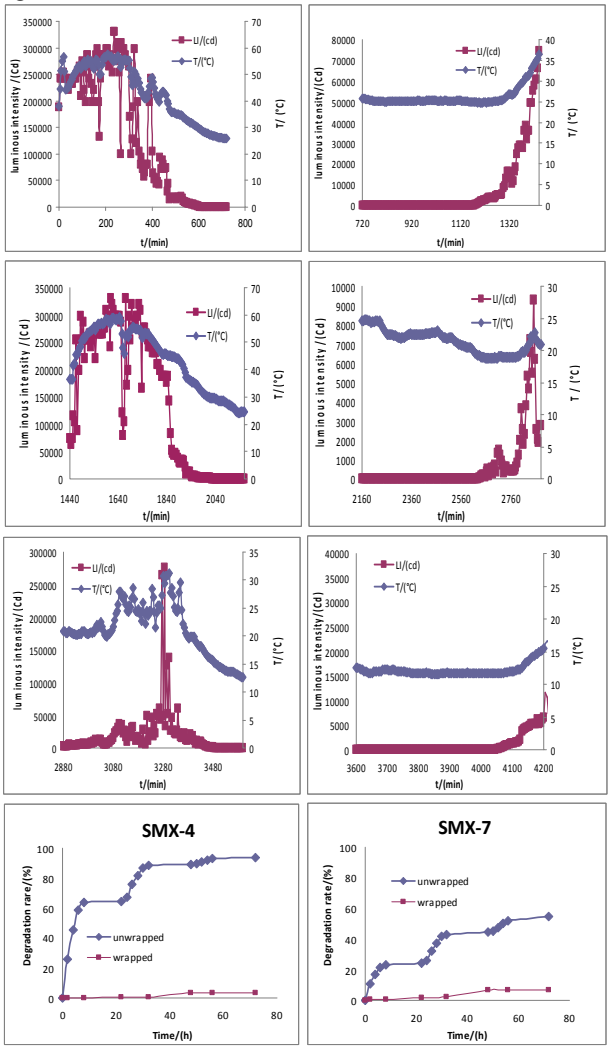


Figure 1. Photodegradation under high pressure mercury lamp

B. *Natural light (daytime and night time)*

The result showed that degradation rates of unwrapped samples were increasing with the elevated temperature for SMX and SPY, and different degradation rates presented at different pH values. Degradation rate of SMX went up to 90% at pH 4, and degradation rate of SPY went up to 60% at pH 7 in 72 h. However, there was still no significant acceleration for TRM degradation towards temperature fluctuation, but thermal hydrolysis was found to be easier to occur in different pH solutions under the circumstance. In unwrapped samples, there were nearly no obvious degradation products occurred to TRM at pH 7 and pH 9, slight degradation products were found at pH 4, while there were obvious degradation products occurred to SPY and SMX. In wrapped samples, hydrolysis products were found for all three antibiotics after 72h, especially for TRM. Temperature and light intensity greatly impacted on the degradation and hydrolysis processes, especially on the thermal hydrolysis of TRM. It also showed the extent of thermal hydrolysis for selected drugs was dependant on pH and time. Data showed degradation of SMX and SPY were fitted to first-order kinetics under sunlight (daytime), but degradation data of TRM were not fitted to the kinetics.



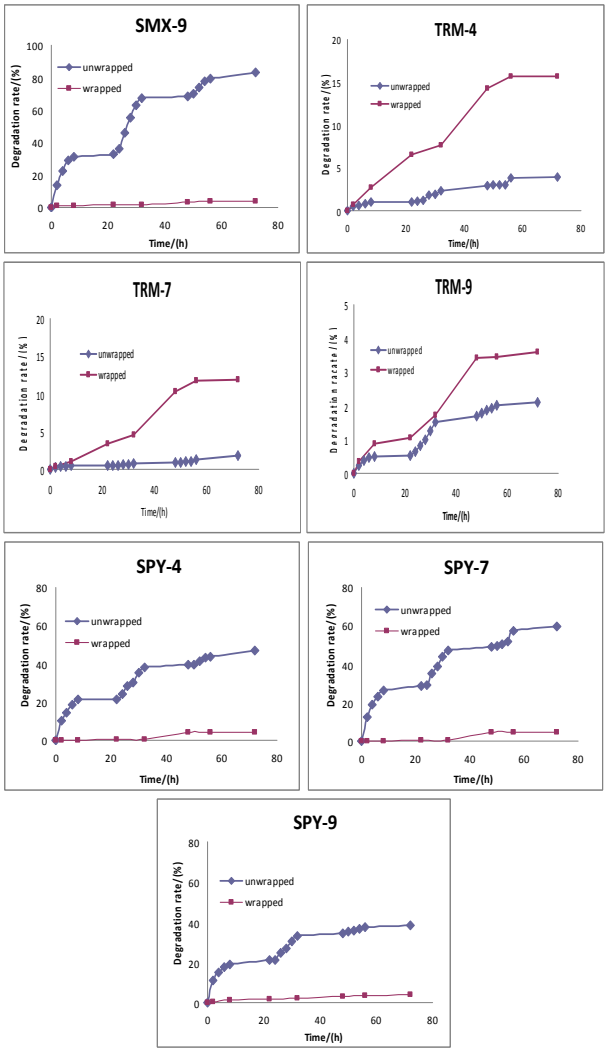


Figure 2. Photodegradaion under natural light

C. *UV degradation*

Fig.3 showed that SMX and SPY were easily degraded under UV condition, while TRM was still very stable. For SMX, degradation rate went up to 98% in 1 h in Fe^{2+} solution, but the degradation rate was slower in HA solution relatively, HA inhibited the degradation rate for SMX compared to other solution. For SPY, the degradation rate in buffer was much faster than in other solutions, it went up to 99% in 8h. However, nearly no degradation happened for TRM in 8h. Also, it demonstrated the removal of sulfonomides was correlated with reductions in ultraviolet absorbance at 240-310 nm. TRM could absorb radiation up to a wavelength of 310 nm, photocatalysis was reported to be an efficient treatment for TRM degradation, cause more •OH radicals generated during the process [14-17]. Degradation data of SMX and SPY were fitted to first-order kinetics, and degradation products occurred during the processes. Control samples showed there was hardly hydrolysis found for each drug in 8h.

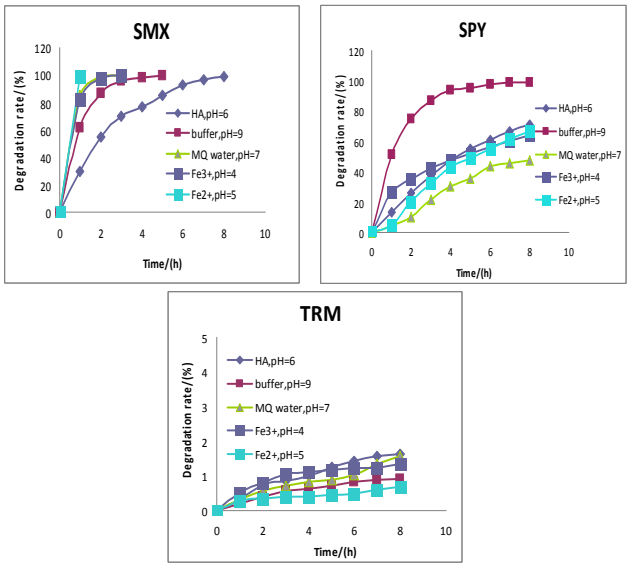


Figure 3. Photodegradation in different media under UV condition

D. *Degradation Pathways of selected antibiotics*

Some reports have reported the probable degradation pathways of sulfononides and trimethoprim under different conditions. For SMX and SPY, the cleavage of the sulfonamide bond and the rearrangement of the aromatic ring represented the main pathways, which involved hydroxyl radical attack either on the benzenic or aromatic rings were proposed in photo-Fenton and ozone degradation [14, 17]. TRM is a relatively stable drug, slight degradation presented in the study, but it could be degraded with catalyst. Abellan investigated the amount of TiO_2 had an important influence on the reaction rate, being improved when the amount of catalyst in solution increased [16]. Sirtori pointed out that the occurrence of various degradation mechanisms for TRM involving an initially slow reaction by direct irradiation and a second faster mechanism induced by the formation of a photoreactive intermediate causing an autocatalytic effect [18]. Hydroxylation, demethylation and cleavage of the original drug molecule were thought as the main degradation routes. An • OH radical conducted mechanism was assumed the main routes of degradation [16, 18].

IV. CONCLUSION

Light source, pH, temperature, time and different aqueous solutions were important to the photodegradation for selected antibiotics. SMX and SPY were easier to degrade under different conditions, but TRM was highly stable to various photolysis. However, thermal hydrolysis was easier to occur for TRM in solution compared to SMX and SPY. Degradation and hydrolysis products were found in the study, whether they are more persistent or not are still not vey clear. Furthermore, the toxic effect of these metabolites for species in the environment should be investigated in the future research.

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