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Degradation of sulfonamides and formation of trihalomethanes by chlorination after pre-oxidation with Fe(VI)

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ABSTRACT

Sulfonamides are used in human therapy, animal husbandry and agriculture but are not easily biodegradable, and are often detected in surface water. Sulfamethazine (SMZ) and sulfadiazine (SDZ) are two widely used sulfonamide antibiotics that are used heavily in agriculture. In this study, they were degraded in an aqueous system by chlorination after pre-oxidation with ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe(VI)), an environmentally friendly oxidation technique that has been shown to be effective in degrading various organics. The kinetics of the degradation were determined as a function of Fe(VI) (0–1.5 mg/L), free chlorine (0–1.8 mg/L) and temperature (15–35°C). According to the experimental results, SMZ chlorination followed second-order kinetics with increasing Fe(VI) dosage, and the effect of the initial free chlorine concentration on the reaction kinetics with pre-oxidation by Fe(VI) fitted a pseudo-first order model. The rate constants of SDZ and SMZ chlorination at different temperatures were related to the Arrhenius equation. Fe(VI) could reduce the levels of THMs formed and the toxicity of the sulfonamide degradation systems with Fe(VI) doses of 0.5–1.5 mg/L, which provides a reference for ensuring water quality in drinking water systems.

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Introduction

Due to their low cost and relatively high efficiency, antibiotics have been widely used in humans and animals to treat and prevent bacterial infections, as medicines and growth promoters (Kümmerer, 2009). Sulfonamides (SNs) are one of the most popular groups of antibiotics, widely used in agriculture and medicine, mainly as antibacterial veterinary drugs (Baran et al., 2009). Because of their incomplete absorption in the body, SNs are excreted in urine and feces and reach wastewater treatment plants, and are detected at varying concentrations in the environment, ranging from nanograms to micrograms per liter (Madureira et al., 2010; Sukul and Spiteller, 2006). These residues in the environment have received widespread

attention, as they may pose potential risks and lead to the development of antibiotic-resistant bacteria. It is essential to investigate green-treatment methods to remove these micro-pollutants (Su et al., 2011). Sulfadiazine (SDZ) and sulfamethazine (SMZ), which are typical synthetic SNs, were chosen in this study to investigate the degradation and toxicity of SNs in water treatment. The structures of SDZ and SMZ are shown in Appendix A Fig.S1.

Various chemical oxidation processes have been applied to remove SNs in water, such as free chlorine, chloramine, and ozone (Dodd and Huang, 2004; Huber et al., 2005; Miao and Tao, 2009). Chlorination has been the most widely used disinfectant in water treatment plants to protect human health for several decades. However, due to their potential

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toxicity and health risks, the formation of disinfection byproducts (DBPs) has raised public concern (Deng et al., 2014; Sedlak and von Gunten, 2011). Limits have been placed on trihalomethanes (THMs) and haloacetic acids (HAAs), which are generated from the reaction of chlorine with organic components in water, in drinking water standards in many countries (Richardson and Ternes, 2014). One of the objectives in this study was to reduce the formation of trihalomethanes in the chlorination process of SNs.

Ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe(VI)) is an emerging water-treatment disinfectant, and is an environmentally friendly iron-containing material (Yates et al., 2014). Fe(VI) is a powerful oxidant (Sharma et al., 2006c). Kinetic assessments of the oxidation of SNs with ferrate showed their effective removal (Sharma et al., 2006b). Unlike the traditional disinfectant treatments, Fe(VI) does not produce secondary pollution. Fe(VI) does not react with bromide ion as ozone does, so Fe(VI) as a pre-oxidant can be effective in decreasing the amounts of DBPs produced during subsequent chlorination (Zhou et al., 2009). There have been some studies on the reactions between Fe(VI) and SNs (Kim et al., 2015; Sharma et al., 2006a). However, water treatment processes are still based on free chlorine disinfection. There is no information available on SN degradation and the formation of THMs in treatment by Fe(VI) followed by chlorination.

The main objectives of this study were to provide a basis for the treatment of wastewater from pharmaceutical factories contaminated by high concentrations of sulfonamide antibiotics by: (1) investigating the influence of Fe(VI) on the degradation of SMZ and SDZ as a function of the concentration of free chlorine and temperature; (2) determining the formation of THMs produced during chlorination of SNs with or without Fe(VI) ; (3) evaluating the evolution of toxicity during the chlorination of SNs with or without Fe(VI) .

1. Materials and methods

1.1. Chemicals

All solutions were prepared with deionized water obtained from a Milli-Q system, with resistivity $>18 \text{ M}\Omega/\text{cm}$. SMZ and SDZ were purchased from Aladdin (Shanghai, China) (purity $>98\%$), which were of reagent grade and used without further purification. Fe(VI) (K_2FeO_4) of high purity ($>96\%$) was obtained in the laboratory by the method of Li et al. (2005) (based on the oxidation of ferric nitrate with hypochlorite). Fe(VI) buffer solutions were prepared by adding $0.005 \text{ mol/L Na}_2\text{HPO}_4$ and 0.001 mol/L borate at pH 9.0 (Bielski and Thomas, 1987), which were used no more than 30 min after preparation. Free chlorine stock solutions were prepared by diluting 5% NaOCl solution (Aladdin). Methanol and acetonitrile used in the high-performance liquid chromatography (HPLC) and gas chromatograph (GC)-electron capture detector (ECD) measurements were of chromatography grade and supplied by Sigma-Aldrich (Shanghai, China). A mixture of four trihalomethanes (THMs, gas chromatographic grade) at a concentration of 10 mg/mL was obtained from Supelco (Supelco Park, USA). Other reagents, including sodium hydroxide (NaOH , analytical grade), sulfuric acid (H_2SO_4 , analytical grade) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, analytical grade)

were obtained from Sinopharm Chemical Reagent (Shanghai, China).

1.2. Analytical procedures

The concentrations of SDZ and SMZ were determined by a HPLC system (Agilent 1200, Agilent, USA) equipped with a C18 column ($150 \times 4.6 \text{ mm}$, $5 \mu\text{m}$) and a UV detector. The mobile phase was a mixture of an 80/20 ratio of 1% (V/V) aqueous acetic acid and methanol (V/V), which was used at a mobile flow rate of 1.0 mL/min . The detector temperature was set at 30°C and the wavelength was set at 265 nm (Bian and Zhang, 2016). The retention time of SDZ was 3.26 min , and the retention time of SMZ was 6.33 min .

The THMs (chloroform, bromoform, bromodichloromethane, and dibromochloromethane) were quantified by GC-ECD (Varian, GC-450, USA) following the method of Li et al. (2016). The GC column was a DB-5 capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, Agilent). The oven for THMs was held at 35°C for 10 min, then was increased at 10°C/min to 80°C , and increased again to 150°C at 20°C/min . The headspace injection and detector temperatures were 210°C and 290°C , respectively. In addition, the limits of quantification (LQD) and limits of detection (LOD) are shown in Appendix A Table S1.

Free chlorine was measured according to the Standard Methods by a UV-1800 spectrometer (Shimadzu, Kyoto, Japan) at a detection wavelength of 510 nm (Gilcreas, 1966).

The toxicity of the samples was tested using a Micro Tox Model 500 Analyzer (Strategic Diagnostic Inc., USA). According to the ASTM Standard Method, the toxicity was assessed with the Microtox “Acute” Toxicity Test and the luminescent bacteria *Vibrio fischeri* (freeze-dried) (Ye et al., 2011). Luminescence was recorded after 15 min of incubation (Mariani et al., 2015). The inhibition of luminescence was calculated by Eq. (1):

$$\text{Inhibition} = \left(\frac{C_0 - C_{15}}{C_0} \right) * 100\% \quad (1)$$

where C_0 is the luminescence intensity of the blank solution (RLU) and C_{15} is the luminescence of samples at 15 min (RLU) (Dong et al., 2017). Each sample was tested in duplicate to ensure accuracy.

1.3. Experimental processes

The experiments used sodium hypochlorite as a disinfectant. The potassium ferrate solids were used to prepare a buffer solution (0.62 mmol/L). Then the buffer solution was added into the reaction mixture ($200 \mu\text{g/L}$ SDZ and $200 \mu\text{g/L}$ SMZ) in a thermostatic water bath so that the initial concentrations of Fe(VI) were 0, 0.5, 1.0, 1.5 mg/L . After stirring for 3 min, a solution of sodium hypochlorite (100 mg/L) was added to give initial free chlorine levels of 0, 0.4, 0.9, 1.4, and 1.8 mg/L . After the experiments started, samples were taken at 0, 1, 3, 5, 7, 10, 12, 15, 20, 25 and 30 min to detect the concentrations of SDZ and SMZ; and after running for certain reaction times (0, 0.25, 0.5, 1, 3, 6 hr), 40 mL samples were collected for GC analysis. All samples were stopped from further reaction with chlorine by adding sodium thiosulfate.

2. Results and discussion

2.1. Chlorine decay

Fig. 1a displays the chlorine decay with different initial free chlorine concentrations after pre-oxidation with Fe(VI) (1.0 mg/L). The concentration of residual chlorine decreased as the reaction proceeded, and the chlorine decay could be divided into two parts: the first hour was a rapid decay process, followed by a steady decay process. In addition, as the initial free chlorine concentration increased, the decay rate of chlorine became slower. When the reaction took place for 6 hr with initial free chlorine concentration of 0.4, 0.9, 1.4 and 1.8 mg/L, the attenuation was 100%, 68.9%, 65.7% and 47.4%, respectively. Due to the fixed amount of sulfonamides in the experiments, the increase in initial free chlorine only increased the rate of degradation. Therefore, the ratio of the attenuation of chlorine decay was smaller at higher initial free chlorine concentration.

The decay of chlorine at a dose of 0.9 mg/L was monitored after pre-oxidation with different doses of Fe(VI) (0.5–1.5 mg/L), as shown in Fig. 1b. When the concentration of Fe(VI) was higher at the same initial free chlorine dose, the decay of chlorine was faster. After 6 hr of reaction, the residual free chlorine concentration with pre-oxidation by Fe(VI) of 0.5, 1.0 and 1.5 mg/L was 0.3, 0.28 and 0.26 mg/L, respectively. Compared with chlorination without pre-oxidation, the decay was faster by 18%, 23% and 26%, respectively. Fe(VI) could oxidize high-molecular-weight organic constituents to low-molecular-weight organic components in water samples (Gan et al., 2015). A higher Fe(VI) dose within the range 0–1.5 mg/L would produce a higher fraction of low-molecular-weight species. This indicated that the sulfonamides would be oxidized into more easily chlorinated components, which consumed more of the free chlorine concentration.

2.2. Degradation kinetics of SDZ and SMZ

2.2.1. Fe(VI)

The degradation of SMZ during chlorination with or without pre-oxidation with Fe(VI) is shown in Fig. 2. The degradation was affected by the variation in Fe(VI) dosage (Fig. 2a). The results showed that the rate of SMZ degradation by chlorination decreased monotonically as the Fe(VI) dosage increased from 0 mg/L to 1.5 mg/L. At Fe(VI) dosages of 0, 0.5, 1.0 and

1.5 mg/L, the degree of SMZ degradation decreased from 100% to 70% after 15 min. As can be seen in Fig. 1b, pre-oxidation with Fe(VI) increased the attenuation of residual free chlorine, which led to a decrease in residual free chlorine available for SMZ degradation. The reactivity of SMZ depended on the free chlorine (Eq. (2)).



The pH values of the water after pre-oxidation with different dosages of Fe(VI) (0–1.5 mg/L) were 7.56, 7.75, 7.82, 8.02. According to Eq. (2), the OCl^-/HOCl ratios were 1.05, 1.62, 1.90 and 3.01, respectively, which reduced the oxidation by the available chlorine in solutes. Therefore, pre-oxidation with Fe(VI) (0–1.5 mg/L) influenced the pH to further affect the chlorination.

Fig. 2b depicts the relationship between time and $-\ln([\text{SMZ}]_t/[\text{SMZ}]_0)$. The pseudo first-order rate constants (k') of the SMZ degradation are shown in Appendix A Table S2. The linear correlation between time and $-\ln([\text{SMZ}]_t/[\text{SMZ}]_0)$ was a satisfactory fit ($R^2 > 0.967$). The reactions of Fe(VI) and SMZ chlorination followed second order kinetics and could be described by Eq. (3).

$$-d[\text{SMZ}]/dt = k''[\text{Fe(VI)}][\text{SMZ}] \quad (3)$$

where k'' represents the apparent second-order rate constant for SMZ degradation with Fe(VI), $[\text{SMZ}]$ ($\mu\text{g/L}$) represents the concentration of SMZ and $[\text{Fe(VI)}]$ (mg/L) represents the total concentration of Fe(VI). Appendix A Fig. S2 shows that the relationship of k'' to the pre-oxidation dosage of Fe(VI) (0–1.5 mg/L) was linear ($R^2 = 0.92$). Therefore, SMZ chlorination with different Fe(VI) dosages followed second-order kinetics.

2.2.2. Free chlorine

Experiments at different free chlorine levels (0.4, 0.7, 10, 1.3 mg/L) were carried out after pre-oxidation with Fe(VI) (1.0 mg/L). The decomposition of SDZ and SMZ is shown in Fig. 3. The results indicate that increasing the initial free chlorine concentration from 0 to 1.9 mg/L enhanced the degradation efficiency within 30 min of reaction for both SDZ and SMZ. Due to the strong oxidizing ability of Fe(VI), 16% of SDZ and 43% of SMZ could be oxidized without free chlorine (Sharma, 2002). Hence, higher free chlorine concentration contributed to better degradation efficiency of SNs.

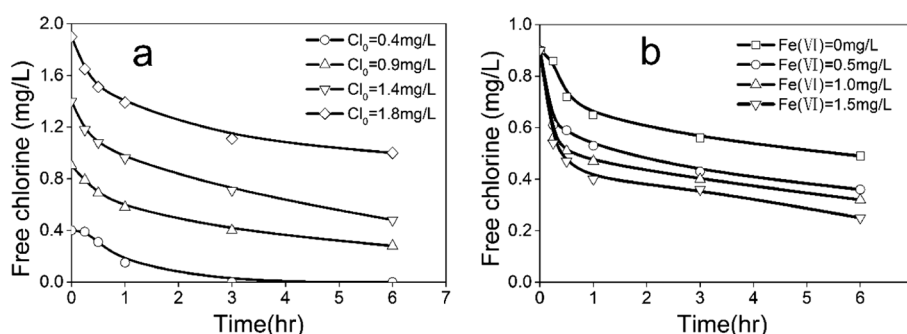


Fig. 1 – Effect of chlorination with or without pre-oxidation with Fe(VI) on residual free chlorine decay. (a) The influence of free chlorine concentrations, (b) the influence of Fe(VI) dosages.

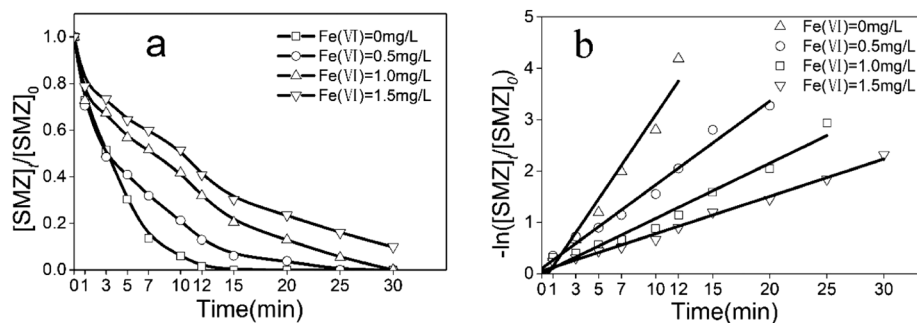


Fig. 2 – Effect of Fe(VI) concentration on the degradation of SMZ with chlorination. (a) Effect of Fe(VI) concentration on the degradation of sulfamethazine (SMZ), (b) pseudo first order kinetics plot of SMZ chlorination. Free chlorine = 0.9 mg/L, Temperature 25°C, pH 7.4, initial SMZ 200 µg/L.

In order to better describe the effect of the initial free chlorine concentration on the reaction kinetics with pre-oxidation by Fe (VI), a pseudo-first order model was applied to depict the degradation of SDZ and SMZ in the first 30 min. The kinetic analysis is shown in Fig. 3c and d. The apparent kinetic rate constant (k_{app}) for the degradation of SDZ and SMZ corresponded to the slopes of the linear fits between $\ln([SNs]_0/[SNs])$ with time. The pseudo first-order rate constants for SDZ and SMZ degradation are shown in Appendix A Table S3. Fig. 3c and d show that the relationship maintained good linearity ($R^2 > 0.97$) in all cases. The results indicated that the degradation of SDZ and SMZ had a satisfactory linear correlation during chlorination after pre-oxidation with Fe(VI).

2.2.3. Temperature

The effect of temperature on the degradation of SDZ and SMZ after pre-oxidation with Fe(VI) (1.0 mg/L) was investigated at 15, 25 and 35°C. Fig. 3a and 3b show that the SDZ degradation efficiency within 30 min increased from 76.1% to 83.4% and SMZ degradation efficiency increased from 92.5% to 100% when the temperature increased from 15 to 35°C. With increasing temperature, the degradation rate became more rapid, which was consistent with Mansour's conclusion (Mansour et al., 2012). Fig. 4c shows that the k_{app} of SDZ decreased from 0.542 sec⁻¹ to 0.432 sec⁻¹ with temperature increasing from 15°C to 35°C, and Fig. 4d shows that the k_{app} of SMZ decreased from 0.122 to 0.078 sec⁻¹.

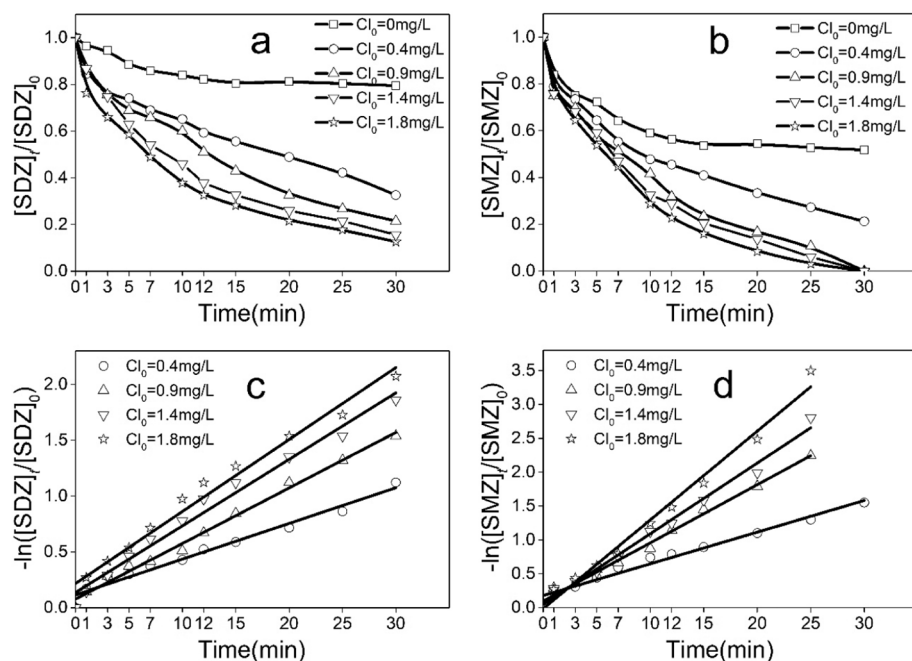


Fig. 3 – Effect of free chlorine concentration on the degradation of sulfadiazine (SDZ) and SMZ after pre-oxidation with Fe(VI) (1.0 mg/L). (a) Effect of free chlorine concentration on the degradation of SDZ, (b) effect of free chlorine concentration on the degradation of SMZ, (c) pseudo first order kinetics plot of SDZ chlorination, (d) pseudo first order kinetics plot of SMZ chlorination. Temperature 25°C, pH 7.4, initial SDZ and SMZ both were 200 µg/L.

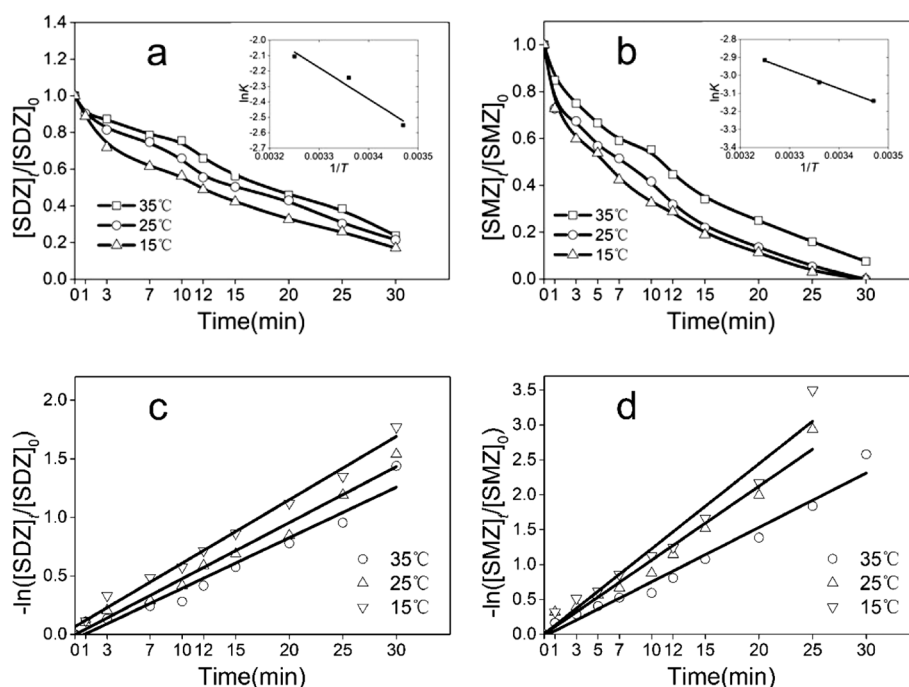


Fig. 4 – Effect of temperatures on the degradation of SDZ and SMZ after pre-oxidation with Fe(VI) (1.0 mg/L). (a) Effect of temperatures on the degradation of SDZ, (b) effect of temperatures on the degradation of SMZ (c) pseudo first order kinetics plot of SDZ chlorination, (d) pseudo first order kinetics plot of SMZ chlorination. Initial free chlorine was 0.9 mg/L, pH 7.4, initial SDZ and SMZ both were 200 µg/L.

According to the apparent kinetic rate constants at different temperatures, the apparent activation energies (E_a) for the degradation of SDZ and SMZ were computed using the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (4)$$

where, R is the ideal gas constant (8.314 J/(mol·K)), and A is the frequency factor.

Fig. 4a and b show that $\ln(k)$ and $1/T$ had a good correlation, with a correlation coefficient (R^2) higher than 0.96. The activation energies of SDZ and SMZ degradation were 8.57 kJ/mol and 16.87 kJ/mol, respectively. When the temperature increased, hypochlorite becomes unstable and more active. Therefore, it was useful to promote the oxidation at a higher temperature.

2.3. Formation of THMs

The formation of total THMs during chlorination, with or without pre-oxidation with Fe(VI), is shown in Fig. 5a. The formation of total THMs was mainly concentrated in the first hour, and stabilized after 3 hr, so the degradation of sulfonamides had almost stopped.

Fe(VI) could effectively reduce the formation of THMs during the following chlorination, in agreement with Gan et al. (2015). As the concentration of Fe(VI) increased, the formation of THMs decreased at the same initial free chlorine dose (0.9 mg/L). When pre-oxidation was carried out with Fe(VI) dosages of 0, 0.5, 1.0 and 1.5 mg/L, the amounts of THMs after a 6-hour reaction were 11.4, 11.2, 8.3 and 5.9 µg/L, respectively. Fe(VI) reduced the levels of THMs from SNs degradation for Fe(VI)

values between 0.5–1.5 mg/L (Fig. 5a). It was possible that Fe(VI) oxidized the sulfonamides, which were highly resistant to chlorine, in the pre-oxidation step (Deborde and Von Gunten, 2008). What's more, Fe(VI) could react with electron-rich organic moieties including phenols, anilines and amines, which were potential THM generators (Lee and von Gunten, 2010). According to previous research, $-SO_2-$ in SDZ and SMZ could be easily eliminated due to the cleavage at the N-S bond, which would generate alcohols and amines after oxidation (Guo et al., 2013). Alcohols showed reactivity with Fe(VI), yielding the formation of aldehydes. Chlorination of alcohols yielded carbonyls, which were converted into chloroform, which was responsible for THM formation (Deborde and Von, 2008). Therefore, the reaction between the sulfonamides and chlorine was responsible for THM formation. Pre-oxidation of alcohols by Fe(VI) could reduce THM formation in the subsequent chlorination.

Fig. 5b depicts the effect of FC concentration on formation of total THMs. The degradation of SDZ and SMZ with Fe(VI) (1.0 mg/L) increased the level of THM formation with increasing free chlorine doses. The concentration of total THMs was stabilized at 2.33 µg/L, 3.97 µg/L, 11.22 µg/L and 12.13 µg/L, respectively, after 6 hr of chlorination. This indicated that the free chlorine concentration was the main factor affecting the formation of THMs.

2.4. Toxicity assessment

Toxicity assessments are very important to determine whether a treatment can produce intermediates that are more toxic than the parent compound (Bonnet et al., 2007). The evolution of

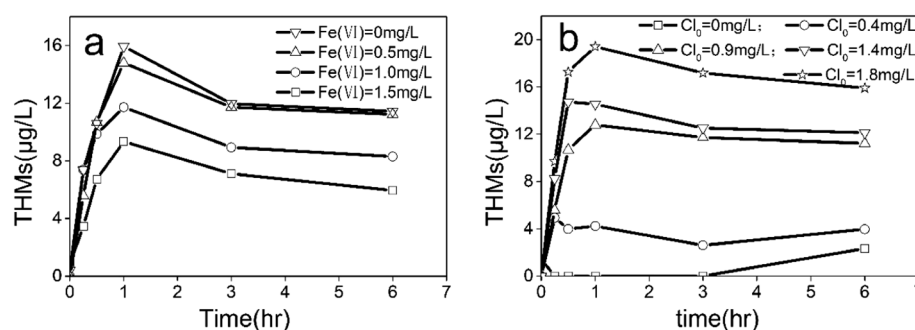


Fig. 5 – The formation of total trihalomethanes (THMs) during chlorination with or without pre-oxidation with Fe(VI). (a) The influence of Fe(VI) dosages, (b) the influence of free chlorine concentrations. Temperature 20°C, pH 7.4, initial SMZ 200 µg/L and initial SDZ 200 µg/L.

toxicity in sulfonamide degradation during chlorination with or without pre-oxidation with Fe(VI) was assessed by the Microtox method. Based on the inhibition of the luminescence by *V. fischeri* marine bacteria, toxicity was measured after contact with samples for 15 min. The results are shown in Fig. 6.

The toxicity resulting from sulfonamide chlorination could be divided into two parts. The toxicity rose rapidly in the first 60 min, which indicated that the formation of some toxic intermediates increased the inhibition of bioluminescence. According to Fig. 5, THMs were formed mainly during the first 60 min. Then, due to the formation of secondary intermediates, the inhibition values continued to rise after 3 hr of chlorination. The toxicity of SMZ towards *V. fischeri* at low concentrations was confirmed, and this trend was consistent with results from a previous study (Dong et al., 2017).

As can be seen in Fig. 6, the inhibition rates with Fe(VI) dosages of 0, 0.5, 1.0 and 1.5 mg/L were 63.02%, 43.85%, 30.29% and 22.08%, respectively. The toxicity of SN degradation with pre-oxidation by Fe(VI) was lower than without pre-oxidation

by Fe(VI), which indicated that Fe(VI) was not only a strong oxidant, but also an environmentally friendly oxidant. In addition, the toxicity decreased as the concentration of Fe(VI) increased. As shown in Fig. 5a, the pre-oxidation with Fe(VI) could reduce the formation of THMs during chlorination, which resulted in a decrease in toxicity. It was indicated that oxidation of the amino group by Fe(VI) could produce less p-aminobenzoic acid, which is a necessary component of the essential vitamin folic acid (Sharma et al., 2006b). Therefore, pre-oxidation by Fe(VI) can reduce the secondary bio-toxicity in water treatment.

3. Conclusions

- (1) As the initial free chlorine concentration increased, the decay rate of chlorine became slower. When the concentration of Fe(VI) was higher with the same initial free chlorine dose, the decay of chlorine was faster.
- (2) The degradation rate of SMZ by chlorination decreased monotonically as the Fe(VI) dosage increased (0–1.5 mg/L). The SMZ chlorination with different Fe(VI) concentrations followed second-order kinetics.
- (3) When the initial free chlorine concentration increased from 0 to 1.9 mg/L, the degradation efficiency of SNs could be enhanced. The effect of the initial free chlorine concentration on the reaction kinetics with pre-oxidation by Fe(VI) fitted a pseudo-first order model.
- (4) With increasing temperature, the degradation rate of SNs became more rapid. The activation energies of SDZ and SMZ degradation were 8.57 kJ/mol and 16.87 kJ/mol, respectively.
- (5) Fe(VI) reduced the levels of THMs during SN degradation for Fe(VI) concentrations between 0.5–1.5 mg/L. The degradation of SDZ and SMZ with Fe(VI) (1.0 mg/L) increased the level of THM formation with increasing free chlorine dose.
- (6) The toxicity of SN degradation with pre-oxidation by Fe(VI) was lower than without pre-oxidation by Fe(VI). The toxicity decreased as the concentration of Fe(VI) increased.

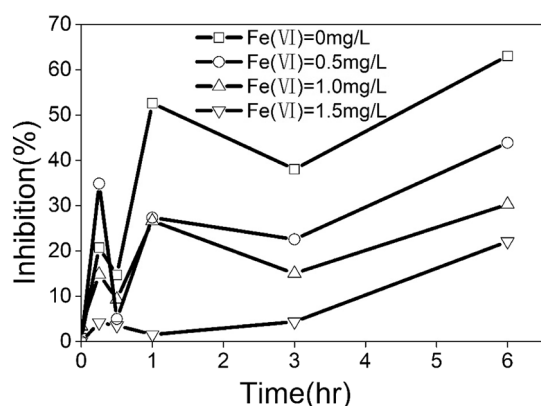


Fig. 6 – Evolution of toxicity of SDZ and SMZ chlorination with or without pre-oxidation with Fe(VI) in terms of inhibition of the luminescence of *Vibrio fischeri* bacteria. Temperature 20°C, pH 7.4, initial SMZ 200 µg/L, initial SDZ 200 µg/L and initial free chlorine 0.9 mg/L.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2018.01.016>.

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