**Original Research** 

# Comparative Study on the Effectiveness of UV/Free Chlorine and UV/H<sub>2</sub>O<sub>2</sub> in Degrading Trimethoprim in Water

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# Abstract

Pharmaceuticals and personal care products (PPCPs) in drinking water have attracted increasing attention from domestic and international scholars, and Trimethoprim (TMP) is one of the common drugs in the aqueous environment. Since reactive substances such as HO• and Cl• and Cl• are generated in the UV/free chlorine oxidation system, it is considered as an emerging alternative to the UV/H<sub>2</sub>O<sub>2</sub> process. However, since the background conditions of the water body and the oxidant concentration have an effect on the oxidation effect, a comparison of the UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> oxidation systems under different conditions was carried out in this paper. It was found that the removal efficiency of TMP by UV/free chlorine was 16% higher than that by UV/H<sub>2</sub>O<sub>2</sub> at an oxidant concentration of 0.05mM, and the removal efficiency of TMP degradation by UV/free chlorine was 17% higher than that by UV/H<sub>2</sub>O<sub>2</sub> oxidation system was superior to the UV/H<sub>2</sub>O<sub>2</sub> oxidation system in degrading TMP. The main reason for this phenomenon is that the quantum yields of HClO and OCl- are higher than those of H<sub>2</sub>O<sub>2</sub>. Under the same UV intensity and concentration conditions, UV/free chlorine oxidation system can produce more free radicals in the same time, so UV/free chlorine oxidation effect is better and less costly.

Keywords: UV/free chlorine, UV/H2O2, advanced oxidation, trimethoprim, quantum yield

## Introduction

Recently, many emerging contaminants have been found in the water environment (e.g. herbicides, odorous substances, pharmaceuticals and personal care products (PPCPs), etc.) [1]. Antibiotics are common PPCPs and

there are now over 10,000 antibiotics widely used to treat and prevent bacterial infections. For example, trimethoprim (TMP) is an antibiotic used primarily to treat bladder infections. However, once released into the water environment, antibiotics can have adverse effects on human health and aquatic ecosystems. This is due to the fact that TMP can enter water bodies through different pathways (e.g., by means of animal excretion, etc.). Although the levels of TMP introduced by these means are low, continuous discharges may have adverse

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effects on terrestrial and aquatic organisms, and these effects may accumulate over time, reaching a point in time when they suddenly manifest themselves irreversibly. On the other hand, it cannot be effectively removed due to the limited degradation capacity of microorganisms. This can lead to the production of more harmful bacteria in the water body, which can cause damage to the water environment. Therefore, it is necessary to remove antibiotics from the water environment. In addition, antibiotics are persistent organic pollutants, so biological treatment processes are not sufficient to degrade antibiotics. Other conventional water treatment techniques (e.g. ozonation absorption) also do not effectively remove antibiotics [2]. Two new advanced oxidation processes, UV/H<sub>2</sub>O<sub>2</sub> and UV/free chlorine, were found to be effective for organic pollution in water [3].

UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process, is an emerging advanced oxidation technology (AOT) proposed by domestic and foreign scholars in recent years. Under the action of UV light, it makes the chemical bonds in H<sub>2</sub>O<sub>2</sub> break and form hydroxyl radicals with high oxidation potential. This radical has high activity and strong oxidation ability, so in the process of water treatment, this advanced oxidation technology can degrade many organic micro-pollutants in the water body that are difficult to degrade [4]. Xia Ping et al. [5]. in the study of ultraviolet/peroxide (UV/H2O2) advanced oxidation process in the application of drinking water, the study showed that the removal efficiency of ultraviolet/ peroxide advanced oxidation degradation of atrazine is 50%, while the degradation and removal efficiency of atrazine under the condition of UV alone is about 40%, so compared with the UV oxidation technology, the advanced oxidation process has certain advantages for the removal of organic micropollutants [6]. However, the UV/H<sub>2</sub>O<sub>2</sub> process has some disadvantages. The low UV absorption and quantum yield of peroxides leads to the need for excessive dosing of peroxides, which increases the chemical cost [7]. In addition, only 5-10% of the peroxide is consumed in the pollutant removal process. Chlorination is often required to quench unreacted peroxides and provide residual disinfectant, which further increases chemical costs. In addition, the UV/  $H_2O_2$  process may alter the formation of disinfection by-products (DBP) during subsequent chlorination, and HO• generated during the UV/H2O2 process may alter the properties of natural organic matter (NOM) present in drinking water. For example, hydroxylation of the generated nitrobenzene leads to the formation of nitrobenzols with higher chlorine reactivity [8]. The oxidation of leucine and serine by HO• also leads to increased halocetic acids (HAA) formation of precursors [9].

The UV/Free chlorine advanced oxidation process has become one of the most promising advanced oxidation process (AOPs). In the UV/free chlorine process, first, UV radiation cuts the HOCl bond to form hydroxyl (HO•) and chlorine radicals (Cl•). HO• is a strong oxidant that reacts non-selectively with organic pollutants at a rate close to diffusion control [10]. Cl• is a selective oxidant that reacts rapidly with compounds containing aromatic rings and double bonds. Subsequently, ClO• and Cl<sub>2</sub>• are produced by complex radical chain reactions, and ClO• and Cl<sub>2</sub>• are also oxide organic compounds. Many studies have reported successful destruction of some persistent organic pollutants (POPs) (e.g., sulfamethoxazole, carbamazepine, diclofenac, benzotriazole, nitrobenzene, trichloroethylene) by UV/free chlorine processes [11]. In addition, UV/free chlorine degrades micropollutants (e.g., trichloroethylene) more effectively than the UV/ H<sub>2</sub>O<sub>2</sub> process (a common UV-based advanced oxidation process) [12]. UV/free chlorine process has two advantages. First, many forms of disinfection require residual chlorine or chloramines (e.g., direct drinking). UV/free chlorine avoids the need for additional added chlorine to quench residual H<sub>2</sub>O<sub>2</sub>. Secondly, for LP mercury lamps emitting at 254 nm, HOCl and OCI- producing radicals, due to the higher molar absorption, may be more effective than parallel processes involving H<sub>2</sub>O<sub>2</sub> in terms of coefficients and quantum yields, reducing the energy demand of pollutants by 30-75% [13].

From previous studies [14], we know that UV/free chlorine advanced oxidation process can reduce the concentration of pollutants in water, but the oxidation effect is affected by various background components in the water body, such as HCO<sub>3</sub><sup>-/</sup>CO<sub>3</sub><sup>2-</sup>, chloride ions, natural organic matter, etc. As an emerging advanced oxidation degradation method based on the generation of Cl•, ClO•, and HO• radicals for oxidation, UV/free chlorine has shown good performance and considerable prospect for the removal of pollutants in the water body. In order to better understand the effect of UV/free chlorine advanced oxidation in degrading organic pollutants in water, it is necessary to compare this oxidation method based on the generation of Cl-, ClO•, and HO•radicals with the current conventional UV/H<sub>2</sub>O<sub>2</sub> based on the generation of HO• radicals. This paper was conducted to investigate the comparison of the removal efficiency of UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation, to examine the effect of oxidant dosing on the action of both advanced oxidation, and the effect of background ions HCO3-/CO32-, chloride ions and natural organic matter in the water column on the degradation of TMP by both UV/H<sub>2</sub>O<sub>2</sub> and UV/free chlorine advanced oxidation systems.

## **Experimental**

## **Experimental Facility**

The UV reactor consists of three parts (as shown in Fig. 1): (1) - closed cardboard large containers, (2) - two 40W low-pressure mercury lamps, producing 254 nm UV light, (3) - magnetic stirrer. The temperature was kept at 25°C. The UV luminous flux ( $I_0$ ) into the



Fig. 1. Experimental facility:UV reactor; 1-ultraviolet lamp, 2-beaker, 3 - magnetic stirring bar, 4-magnetic stirrer.

solution was determined to be 0.567  $\mu$ Es<sup>-1</sup> using iodide/ iodate chemophotometry. The volume of the UV reactor was 0.6 L, so the UV intensity (PUV) was determined to be 9.45×10<sup>-7</sup> Einstein/L-s. The effective path length (L) was determined to be 3.01cm by measuring the kinetics of dilute H<sub>2</sub>O<sub>2</sub> photolysis. The mean UV injection rate (EP<sub>0</sub>) was estimated to be 0.0028  $\mu$ E<sup>-1</sup>cm<sup>-2</sup>.

### **Experimental Material**

The experimental substances main are (1) trimethoprim (TMP) (98%) (2) methanol (3) natural organic matter (NOM) (4) sodium thiosulfate (5) sodium hypochlorite (6) sodium dihydrogen phosphate, etc. Ultra-pure water was used in the experiments unless otherwise stated. Ultra-pure water was prepared by ultra-pure water machine (MillI-Q), and the resistivity of the prepared ultra-pure water was 18.2 M $\Omega$ ·cm. The natural organic matter (NOM) used in this study is the standard natural organic matter of the International Humic Acid Association, model: Suwannee River NOM (No. 2R101N). The configuration was done by dissolving 500 mg of natural organic matter in ultrapure water, followed by sufficient stirring to dissolve it, and after 24 hours, it was filtered using a glass fiber membrane (0.45 micron) and finally calibrated with a total organic carbon tester.

# **Experimental Methods**

To prepare the TMP stock solution, 0.01mM TMP was added to 1000 ml of water. The UV lamp was turned on for 60 min for preheating before the start of the experiment. Add 500 mL of TMP solution to the beaker near the UV lamp, then add the 0.05 mM $\sim$ 0.2 mM of sodium hypochlorite solution to

the test solution containing 2 mM phosphate buffer. Heat the solution to 25°C. pH control with phosphate buffer solution. The magnetic stirrer was set to a speed of 400 r/min. UV lamp turned by automatic switch to irradiate the solution for 20 minutes. A 1mL solution sample was collected at various time intervals over 20 min, and then a few drops of 0.1 M sodium thiosulfate were added to the solution sample to terminate the reaction between the free radical and TMP. Both experimental protocols for UV/H<sub>2</sub>O<sub>2</sub>, UV/free chlorine were performed under the same experimental conditions, same light intensity, same room temperature, oxidant concentration, and the experiments for free chlorine alone were performed in a similar manner without UV light. The calculation of the removal efficiency for TMP is shown in Equation (1) where  $C_0$  represents the initial concentration of TMP and  $C_1$ represents the concentration of TMP at time t. To make the experimental data more accurate, the experiment was repeated three times and the average of the three sets of data was taken to eliminate the error. Then, the data were counted by standard deviation method.

Removal efficiency of TMP(%) = 
$$\frac{C_0 - C_t}{C_0} \times 100\%$$
 (1)

## TMP Analysis Method

The concentration of TMP was determined by high performance liquid chromatography. The column was a symmetric C18 column with 0.3% acetonitrile and acetic acid as mobile phases. The volume ratio of acetonitrile to acetic acid is 20:80. The detection wavelength was 280 nm, the flow rate was 1.0 mL/min, and the column temperature was 28°C [15].

## Determination of H,O, Concentration

The concentration of hydrogen peroxide is measured by the DPD (dimethylparaphenylenediamine) colorimetric method. The main principle of the DPD colorimetric method is that when the catalyst horseradish peroxidase (POD) is present in the solution, H<sub>2</sub>O<sub>2</sub> oxidizes POD and the ensuing oxidation product oxidizes DPD to the cationic group DPD.+. DPD.+ is a red colored compound, which has a strong absorbance and was measured by UV-Vis spectrophotometer at a wavelength of 551 nm. The specific assay procedure is as follows: first, prepare a 10mL cuvette, then add 1 mL of phosphate buffer solution with a concentration of 0.5 M to it, then add 3mL of the sample to be measured, dilute the solution to 10 mL and pour it into a 3 cm cuvette, then quickly add 50 µL of DPD solution and mix it for 15 seconds, mark it as zero at 551 nm with a UV-Vis spectrophotometer, then add 50  $\mu$ L of POD solution was added and mixed well for 50 seconds, and the absorbance at 551nm was measured by UV-visible spectrophotometer [16].

## **Results and Discussion**

# Comparison of the Degradation Efficiency of Different Reaction Conditions

## Comparison of Degradation Efficiency at Different Oxidant Dosing Amounts

Figs 2(a, b) show the degradation of TMP by UV/ $H_2O_2$  and UV/free chlorine under different oxidant concentration conditions, expressed as the concentration of TMP remaining after the process to the initial concentration. When the concentration of oxidant is 0.05mM, the removal efficiency of TMP degradation by UV/ $H_2O_2$  advanced oxidation process is 71%, while the removal efficiency of TMP degradation by UV/ $H_2O_2$ ; when the concentration of oxidant is 0.10 mM, the removal efficiency of TMP degradation by UV/ $H_2O_2$ ; when the concentration of oxidant is 0.10 mM, the removal efficiency of TMP degradation by UV/ $H_2O_2$ ; when the concentration of oxidant is 0.10 mM, the removal efficiency of TMP degradation by UV/ $H_2O_2$  advanced oxidation process is 81.2%, while the removal efficiency of TMP degradation by UV/ $H_2O_2$ . When the oxidant concentration was



Fig. 2. Degradation of TMP under different oxidant concentration conditions; a) UV/free chlorine, b) UV/ $H_2O_2$ 

Experiment condition:  $[TMP]_0 = 0.01 \text{ mM}$ , [free chlorine]\_0 = 0.05 mM~0.2 mM,  $[H_2O_2]_0 = 0.05 \text{ mM}~0.2 \text{ mM}$ , PUV = 9.45×10<sup>-7</sup> Einstein/L-s, pH = 7.2. 0.10 mM, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 81.2%, while the removal efficiency of TMP degradation by UV/free chlorine was 93%, which was 11.8% higher than that by  $UV/H_2O_2$ ; when the oxidant concentration was 0.15 mM, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 83%, while the removal efficiency of TMP degradation by UV/free chlorine was 94%. When the oxidant concentration was 0.20 mM, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 84%, while the removal efficiency of TMP degradation by UV/free chlorine was 96%, which was 12% higher than that of UV/H<sub>2</sub>O<sub>2</sub>. The removal efficiency and degradation rate of TMP by UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> increased with the increase of oxidant concentration, and the removal efficiency of TMP by UV/free chlorine was higher than that by UV/H2O2 under the same oxidant concentration, but the degradation rate did not increase linearly with the increase of oxidant concentration.

This is due to the fact that it has been reported in the relevant literature that the molar absorbance coefficient of H<sub>2</sub>O<sub>2</sub> is 18 M<sup>-1</sup>cm<sup>-1</sup> and the quantum yield of H<sub>2</sub>O<sub>2</sub> is 0.5. The quantum yields of HOCl and OCl- at a wavelength of 254 nm and room temperature were 1.45 and 0.97, respectively, and the quantum yield of HOCl was 2.9 times that of H<sub>2</sub>O<sub>2</sub>, while that of OCl- was 1.94 times [17]. Therefore, the quantum yield of UV/free chlorine is higher than that of UV/  $H_2O_2$  under the same initial conditions, the same UV concentration, and the same oxidant concentration. Meanwhile, the degradation rate constants of [HO•], [Cl•], and [ClO•] reactions with TMP are all of the same order of magnitude, so the UV/free chlorine oxidation system is more effective than UV/H<sub>2</sub>O<sub>2</sub> oxidation system in degrading TMP under the same conditions. In addition, when the oxidant concentration was increased from 0.05 mM to 0.10 mM, the removal efficiencies of UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> increased by 10% and 6%, respectively, but when the oxidant concentration was increased from 0.10mM to 0.15 mM, the removal efficiencies only increased by 1% and 2%. The degradation rate did not maintain a linear increase with increasing target concentration. This is due to the fact that as the concentration of oxidant increases, the number of reactive substances (radicals) generated per unit time increases, and the chance of reaction between radicals increases, and the radicals do not hold a linear growth to react with TMP, so the degradation rate does not hold a linear growth as the concentration of oxidant increases.

## Comparison of Degradation Efficiency at Different pH

Fig. 3 shows the comparison of the degradation effect of two advanced oxidation systems, UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub>, on TMP after 10 min of oxidation under different pH conditions. As can be seen from the figure,



Fig. 3. Comparison of UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> degradation under different pH. Experiment condition:  $[TMP]_0 = 0.01 \text{ mM}, [H_2O_2]_0 = [free chlorine]_0 = 0.05 \text{ mM}, PUV = 9.45 \times 10^{-7} \text{ Einstein/L-s.}$ 

at pH 6.1, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 80.1%, while the removal efficiency of TMP degradation by UV/free chlorine was 93.4%, which was 13.3% higher than that by  $UV/H_2O_3$ ; at pH 7.2, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 79.3%, while the removal efficiency of TMP degradation by UV/free chlorine was 94%, which was 14.7% higher than that by UV/H<sub>2</sub>O<sub>2</sub>. At pH 8.2, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 58.5%, while the removal efficiency of TMP degradation by UV/free chlorine was 81.1%. The removal efficiency of TMP degradation by UV/free chlorine was 81.1%, which was 22.6% higher than that of UV/H<sub>2</sub>O<sub>2</sub>. Therefore, when the pH was in the range of 6-9, the removal efficiency of TMP degradation by UV/free chlorine decreased gradually with the increase of pH, and the degradation rate of TMP by UV/free chlorine was higher than that of TMP by UV/H<sub>2</sub>O<sub>2</sub> under the same test conditions. According to the relevant literature [18], the quantum yield of UV/H<sub>2</sub>O<sub>2</sub> was independent of pH for  $H_2O_2$  concentrations in the range of  $2 \times 10^{-5}$ to 0.1 M. Therefore, the effect of quantum yield on the degradation effect of advanced oxidation under different pH conditions was excluded.

The main reasons for the effect are: (1) In this test, phosphate buffer solution was used, and under acidic conditions, the main form of phosphate buffer solution is  $H_2PO_4^{-}$ , while under alkaline conditions, the main form of phosphate buffer solution is  $HPO_4^{-2-}$ , and according to the relevant literature, the reaction rate constant of HO• and  $H_2PO_4^{-1}$  is  $2\times104$  M<sup>-1</sup>S<sup>-1</sup>, and the reaction rate constant of HO• and  $HPO_4^{-2-}$  is  $1.5\times105$  M<sup>-1</sup>S<sup>-1</sup>, which is 75 times of the reaction rate constant of HO• and H\_2PO\_4^{-2-} is constant of HO• and H\_2PO\_4^{-2-} is  $1.5\times105$  M<sup>-1</sup>S<sup>-1</sup>, which is 75 times of the reaction rate constant of HO• and H\_2PO\_4^{-2-} in the phosphate conditions, a large amount of HPO\_4^{-2-} in the phosphate

buffer solution and the target pollutant TMP in the experiment produced a competitive mechanism that consumed a portion of the HO•. (2) In the  $UV/H_2O_2$ advanced oxidation system, the redox potential of the hydroxyl radical gradually decreases with increasing pH. At pH 3, the redox potential of HO• was 2.62 V, at pH 5, the redox potential of HO- was 2.51 V, at pH 7, the redox potential of HO• was 2.39 V, at pH 9, the redox potential of HO• had a redox potential of 2.29 V at pH 11, a redox potential of 2.15 V at pH 11, and a redox potential of 2.15 V at pH 11. In addition, it has been reported in the literature that when the pH is strongly alkaline, there is a certain concentration of HO<sub>2</sub><sup>-</sup> in the UV/H<sub>2</sub>O<sub>2</sub> reaction system, which has a certain trapping effect on HO• and the secondary reaction rate constant is large, so some of the HO• is consumed, and the above two reasons make the degradation efficiency of both UV/free chlorine and UV/H2O2 on TMP under alkaline conditions reduced.

In a study on the degradation of atrazine by UV/free chlorine, Xiujuan Kong showed that the degradation efficiency of atrazine by UV/free chlorine and  $UV/H_2O_2$  was comparable at pH 7 and 9, but the degradation efficiency of atrazine by UV/free chlorine at pH 5 was significantly higher than that of atrazine by  $UV/H_2O_2[19]$ . Unlike the present study, the degradation efficiency of TMP by UV/free chlorine was higher than that of UV/H<sub>2</sub>O<sub>2</sub> under acidic and neutral conditions, while the degradation efficiency of atrazine by UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> was comparable. In a study of the advanced oxidative degradation of typical organic for pollutants by UV persulfate, it was shown that the degradation rate of iodoacetic acid in the UV/H<sub>2</sub>O<sub>2</sub> degradation system decreased sharply when the pH increased to 11.

Comparison of the Degradation Efficiency of Different Water Background Conditions

## Comparison under Different HCO<sub>3</sub><sup>-/</sup>CO<sub>3</sub><sup>2-</sup> Concentration Conditions

Fig. 4 shows the comparison of the TMP removal efficiencies between UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> after 10 min of oxidation at pH 7.1 and different  $HCO_3^{-}/CO_3^{-2}$  concentrations. As shown in the figure, after degradation by advanced oxidation, the removal efficiency of TMP by UV/H2O2 advanced oxidation process was 78% when the HCO<sub>3</sub><sup>-/</sup>CO<sub>3</sub><sup>2</sup>-concentration was 0mM, while the removal efficiency of TMP by UV/free chlorine was 94%, which was 16% higher than that by UV/H<sub>2</sub>O<sub>2</sub>. When the HCO<sub>3</sub><sup>-/</sup>CO<sub>3</sub><sup>2-</sup> concentration was 1 mM, the removal efficiency of TMP by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 75%, while the removal efficiency of TMP by UV/free chlorine was 92%, which was 17% higher than that by UV/H<sub>2</sub>O<sub>2</sub>. When the HCO<sub>3</sub>/CO<sub>3</sub><sup>2</sup>-concentration was 2 mM, the removal efficiency of TMP by UV/H2O2 advanced oxidation



Fig. 4. Comparison of UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> degradation under different  $HCO_3^{-7}/CO_3^{-2-}$  concentrations

Experiment condition:  $[TMP]_0 = 0.01 \text{ mM}, [H_2O_2]_0 = [\text{free chlorine}]_0 = 0.05 \text{ mM}, \text{PUV} = 9.45 \times 10^{-7} \text{ Einstein/L-s.} [HCO_3^{-7}/CO_3^{-2}] = 0 \text{ mM} \sim 3 \text{ mM}.$ 

process was 74%, while the removal efficiency of TMP by UV/free chlorine was 88%, which was 14% higher than that by UV/H<sub>2</sub>O<sub>2</sub>. When the  $HCO_3^{-2}/CO_3^{-2}$ concentration was 3 mM, the removal efficiency of TMP by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 71%, while the removal efficiency of TMP by UV/free chlorine was 84%, which was 13% higher than that by UV/H<sub>2</sub>O<sub>2</sub>. In addition, the degradation of TMP by both UV/free chlorine and UV/H2O2 advanced oxidation processes decreased with increasing HCO3<sup>-</sup>/CO3<sup>2</sup>concentration, but the effect was not significant, as the HCO<sub>2</sub><sup>-/</sup>CO<sub>2</sub><sup>2-</sup> concentration increased from 0 to 1mM, the removal efficiency of UV/H2O2 advanced oxidation process decreased only 3%, and the removal efficiency of UV/free chlorine advanced oxidation process decreased only 2%.

For the degradation of TMP, both advanced oxidation methods showed some degradation under the condition of containing certain concentration of HCO<sub>3</sub><sup>-/</sup>CO<sub>3</sub><sup>2-</sup>, but the removal efficiency of TMP by UV/free chlorine was significantly higher than that by UV/H<sub>2</sub>O<sub>2</sub>. This is due to the molar absorption coefficient of H2O2 of 18 M-1 cm-1 and the quantum yield of H<sub>2</sub>O<sub>2</sub> of 0.5. The quantum yields of HOCl and OCI- at 254 nm and room temperature are 1.45 and 0.97, respectively, and the quantum yield of HOCl is 2.9 times the quantum yield of  $H_2O_2$ , while the quantum yield of OCl- is 1.94 times the quantum yield of H<sub>2</sub>O<sub>2</sub>. Therefore, the quantum yield of UV/free chlorine is higher than that of UV/H2O2 under the same initial conditions, the same UV concentration, and the same oxidant concentration. Meanwhile, the degradation rate constants of [HO•], [Cl•], [ClO•] and TMP reactions are all of the same order of magnitude, so the UV/free chlorine oxidation system degrades TMP better than

the  $UV/H_2O_2$  oxidation system under the same conditions.

There was a slight decrease in the degradation rate with increasing  $HCO_3^{-7}/CO_3^{2-}$  concentration, due to the consumption of reactive radicals by  $HCO_3^{-7}/CO_3^{2-}$ , which follows from the Equations (2) to (4).

$$Cl_{\bullet} + HCO_{3}^{-} \rightarrow HCl_{\bullet} + CO_{3}^{-}$$
  
 $k = 2.2 \times 108 M^{-1} s^{-1} [20]$  (3)

$$\begin{aligned} \text{Cl}_{2}\bullet^{-} + \text{HCO}_{3}^{-} &\to \text{CO}_{3}\bullet^{-} + 2\text{Cl}^{-} + \text{H}^{+} \\ k &= 8.0 \times 107 \text{M}^{-1}\text{s}^{-1} \ \text{[20]} \end{aligned} \tag{4}$$

The reaction rate constant k is taken from the literature [20].

The rate constants for the secondary reactions of HO• and HCO<sub>3</sub><sup>-</sup> are  $k = 8.5 \times 10^6 M^{-1} s^{-1}$ ; for Cl• and HCO<sub>3</sub><sup>-</sup> are  $k = 2.2 \times 108 M^{-1} s^{-1}$ ; for  $Cl_{2} \cdot and HCO_{3}^{-1}$  are k = 8.0 $\times$  10<sup>7</sup>M<sup>-1</sup>s<sup>-1</sup>. But the generated CO<sub>3</sub>• reacts very quickly with organic compounds containing amine groups (e.g. TMP). It has been reported in the relevant literature that the rate constant of the secondary reaction between  $CO_3^{\bullet}$  and TMP is 3.45×107 M<sup>-1</sup>s<sup>-1</sup>, so when a certain concentration of HCO3<sup>-</sup>/CO3<sup>2-</sup> exists in the solution, although some of the free radicals are consumed by  $HCO_{2}^{-}/CO_{2}^{-}$  is consumed, the new radical  $CO_{2}^{-}$ produced will also react with TMP, thus compensating for the oxidation of part of the consumed radical [21]. Therefore, the degradation efficiency of TMP by both UV/free chlorine and UV/H2O2 advanced oxidation processes decreased only slightly with the increase of  $HCO_3^{-}/CO_3^{-2}$  concentration in the solution.



Fig. 5. Comparison of UV/free chlorine and UV/ $H_2O_2$  degradation under different NOM concentrations. Experiment condition:  $[TMP]_0 = 0.01mM$ ,  $[H_2O_2]_0 =$ 

 $[\text{free chlorine}]_0 = 0.05 \text{ mM}, \text{ PUV} = 9.45 \times 10^{-7} \text{ Einstein/L-s} [\text{NOM}]_0 = 0 \text{ mg/L} \sim 5 \text{ mg/L}.$ 

# Comparison of Degradation Efficiency under Different NOM Concentration Conditions

Fig. 5 shows the comparison of the degradation of TMP by two advanced oxidation systems, UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub>, after 10 min of oxidation under neutral conditions at NOM concentrations of 1 mg/L, 3 mg/L and 5 mg/L, respectively. As shown in the figure, after degradation by advanced oxidation, the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process with and without NOM was 74.3%, while the removal efficiency of TMP degradation by UV/free chlorine was 92.0%, which was 17.7% higher than that by UV/H<sub>2</sub>O<sub>2</sub>; the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process with 1 mg/L NOM was 68.2%, while the removal efficiency of TMP degradation by UV/free chlorine was 86.8%, which was 18.7% higher than that by UV/H2O2. The removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 68.2% at 1 mg/L NOM, while the removal efficiency of TMP degradation by UV/free chlorine was 86.8%, which was 18.6% higher than that by  $UV/H_2O_2$ ; the removal efficiency of TMP degradation by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 61.8% at 3 mg/L NOM, while the removal efficiency of TMP degradation by UV/free chlorine was 61.8%, which was 18.6% higher than that by UV/H2O2. The removal efficiency of TMP degradation by UV/free chlorine was 77.5%, which was 15.7% higher than that by UV/H<sub>2</sub>O<sub>2</sub>; at 5mg/LNOM, the removal efficiency of TMP degradation by UV/ H<sub>2</sub>O<sub>2</sub> advanced oxidation process was 57.3%, while the removal efficiency of TMP degradation by UV/free chlorine was 72.6%, which was higher than that by  $UV/H_2O_2$ . 72.6%, which is 15.3% higher than  $UV/H_2O_2$ .

In both advanced oxidation processes of UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> degradation of TMP, the presence of NOM inhibited both advanced oxidation systems of TMP degradation when the NOM concentration was in the concentration range of 1-5mg/L, and the inhibition increased with the increase of the NOM concentration. Kong et al showed in a study of atrazine degradation by UV/free chlorine that more than 90% of atrazine was removed by the UV/free chlorine oxidation system in the absence of NOM in the solution, and the degradation efficiency decreased when a certain concentration of NOM was present in the solution, with the removal efficiencies decreasing to 88%, 70% and 60% for NOM concentrations of 1 mg/L, 3 mg/L and 5 mg/L, respectively.

The main reasons for this phenomenon are: (1) the secondary reaction rate constant of NOM and HO• is  $2.5 \times 104 \text{ M}^{-1}\text{S}^{-1}$ , and the secondary reaction rate constant of NOM and Cl• is  $1.3 \times 104 \text{ M}^{-1}\text{S}^{-1}$ . When NOM is present in the solution, NOM and the target pollutant jointly compete for reactive radicals, resulting in some of the reactive radicals not interacting with the target pollutant and reducing the oxidation efficiency. (2) NOM has a certain light absorption effect, and the molar

absorption coefficient of NOM is 0.041 (mg-C/L)<sup>-1</sup>cm<sup>-1</sup>; therefore, through two effects, the presence of NOM reduces the removal efficiency of advanced oxidative degradation of TMP.

## Conclusions

(1) The degradation of TMP by UV/free chlorine advanced oxidation is better than that by UV/H<sub>2</sub>O<sub>2</sub>, mainly because the quantum yields of HCIO and OClare higher than those of H<sub>2</sub>O<sub>2</sub>, and the concentration of free radicals produced by free chlorine is higher than that by H<sub>2</sub>O<sub>2</sub> under the same dosage of oxidant. At the same time, increasing the dosage of free chlorine and H<sub>2</sub>O<sub>2</sub> can increase the concentration of free radicals generated in the two advanced oxidation systems and improve the oxidation efficiency of the target pollutants, so as to effectively improve the removal efficiency of TMP by both UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation systems.

(2) When a certain concentration of  $HCO_3^{-7}CO_3^{-2}$  was present in the solution, there was a slight decrease in the degradation efficiency of both UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation systems for the target pollutants. This is because the presence of  $HCO_3^{-7}CO_3^{-2}$  in the solution consumes [HO•], [Cl•], [ClO•], etc. in the UV/free chlorine oxidation system and HO• in the UV/H<sub>2</sub>O<sub>2</sub> oxidation system. However, the generated  $CO_3^{-}$ , a selective radical, undergoes a rapid oxidation reaction with TMP, an organic micropollutant containing amino groups, thus compensating for part of the reduced degradation efficiency of TMP due to the consumption of free radicals.

(3) When a certain concentration of NOM was present in the solution, the degradation efficiency of both UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation systems for the target pollutant TMP gradually decreased as the concentration of NOM increased. The main reasons for this phenomenon are: the NOM and the target pollutant compete for reactive radicals, resulting in some of the reactive radicals not interacting with the target pollutant, and the NOM has a certain light absorption effect, which reduces the utilization of UV light.

(4) The degradation of TMP by two advanced oxidation systems, UV/free chlorine and UV/H<sub>2</sub>O<sub>2</sub>, was inhibited when the pH of the solution was alkaline. Under alkaline conditions, the main form of phosphate buffer solution present is  $HPO_4^{2-}$ , which consumes a portion of the HO•. In addition, in the advanced oxidation system, the redox potential of the hydroxyl radical gradually decreases with increasing pH.

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# **Conflict of Interest**

The authors declare no conflict of interest.

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