Degradation of Triclosan by Co-exposure to Chlorine Dioxide and UV Irradiation

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Abstract. This study investigated the effect of water quality parameters during simultaneous chlorine dioxide disinfection and low pressure ultraviolet (LPUV) irradiation on TCS degradation. The TCS degradation by the co-exposure process was sensitive to chlorine dioxide dosage, concentration of TCS, pH, and NOM. The removal efficiency increases as the pH increases. Neutral and slightly alkaline environments is conductive to promote TCS elimination. The removal rate within 1 minute of pH 5 was only 95.02%. The smaller the removal rate of TCS was decreased as the concentration of humic acid increasing. The higher the concentration of TCS lead to the lower the experimental removal. 2,4-DCP was generated during UV/ClO2, ClO2 and UV, however, the production of 2,8-Cl2DD was not detected during UV/ClO2 process.

1. Introduction
Triclosan (TCS) as personal care products (PPCPs) is a popular international broad spectrum antimicrobial agent widely used in many personal care products, as well as consumables, potentially serious harm. Studies have shown that under certain conditions, TCS also produces strong carcinogenic dioxin during photocatalytic degradation[1]. And according to the monitoring, the concentration of TCS in the sewage discharged from the sewage plant ranges from 0.02μg/L to 2.7μg/L[2]. Linpeng Li et al. showed[3] that TCS can cause DNA breakage damage in cells caused by great damage to normal human stem cells, and there is a clear correspondence between time and dose. Therefore, it is necessary to study the effective removal of TCS.

UV/ClO2 is a new type of drinking water treatment process that uses hydroxyl radicals generated by UV light to remove organic matter from water together with chlorine dioxide, which can reduce by-product production[4]-[5]. This experiment uses the UV/ClO2 process to remove TSC from drinking water, providing basic experiments for practical applications[6]-[8].

2. Materials and methods

2.1. Experimental reagents and instruments
TCS (99.0%, Dr.Ehrenstorfer), Stabilized chlorine dioxide solution and its activation solvent (Hach), Sodium thiosulfate pentahydrate (AR), Sodium hydroxide (AR), Hydrochloric acid (AR), Methanol (Anpel), Acetonitrile (Anpel), Humic acid (AR), Chlorine dioxide reagent (Glycin reagent and DPD free Chlorine powder pillow bag, American hach), HC-C18 small column (Anpel), Hexane (Anpel), LC-20A high performance liquid chromatography (Shimadzu, Japan); magnetic stirrer (Dr),
Germany; pH meter (Eutech); DR2800 spectrophotometer (Hach Company, USA); GC-MS (Shimadzu, Japan); Millipore Pure water meter (millipore, USA); solid-liquid extraction device (Suplco, USA); UV lamp (20W, main wavelength 254nm).

2.2. Experimental method
First, 2L of TCS(400µg/L) stock solution was taken into the reaction generator and mix well. Then, when adding UV light irradiation conditions, pour the prepared chlorine dioxide solution into the reaction. Then, start the reaction. A series of 10 mL of samples were taken out periodically, and the residual free chlorine was quenched immediately by excess sodium thiosulfate at a molar ratio of Na2SO3 to chlorine of 1.2 to 1. All experiments were conducted in triplicate, and the relative standard deviations of all data points were determined to be less than 10%.

2.3. Analysis method
The column was an Inertsil® ODS-SP column (4.6×250 mm. ID, 5 µm); the mobile phase was isocratically eluted with acetonitrile : water = 70%:30% solution at a flow rate of 0.8 mL/min. Column temperature 35ºC, SPD-M20A detector (wavelength range 190 ~ 800nm), detection wavelength is 230nm, injection volume 10µL.

3. Results and analysis

3.1. UV, ClO2 and UV/ ClO2 remove TCS
Comparative elimination of TCS by UV, chlorine dioxide and co-exposure to UV and chlorine dioxide was shown in Figures 1.

![Figure 1. Comparison of UV, ClO2 and UV/ ClO2 removal of TCS](image)

As you can see from figure 1, under three different process conditions, the removal effect of TCS is: UV/ClO2 > ClO2 > UV, the degradation of TCS by UV can reach to 90% in 60min. Chlorine dioxide alone could degraded TCS effectively and removed 80% of TCS in 1 min. UV/ ClO2 has the best degradation effect on TCS, when co-exposure to UV and chlorine dioxide, while approximately 99% of TCS was removed in 1min.

3.2. Effect of pH on TCS removal
The influence of pH on TCS elimination during co-exposure to UV and chlorine dioxide was investigated under five different pH conditions (i.e., 5,6,7,8 and 9) (Figure 2).
As shown in Figure 2, when the pH is 5 within 30s, the removal effect of chlorine dioxide and ultraviolet light on TCS is obviously not as good as several others. The removal rate is relatively low, and the removal effect is very good at pH 6, 7, 8, or 9, and the reaction is almost completed within a short 10s. Studies have shown that the oxidation ability of chlorine dioxide is basically not affected by the pH value, and it has strong disinfection ability in the range of pH 6~10\cite{9}. This effect indicates that the removal of TCS by the UV and chlorine dioxide process has a good effect when the TCS solution is weakly acidic or weakly alkaline.

3.3. Effect of ClO$_2$ on TCS removal

Figure 3 displays the effect of chlorine dioxide dosages (0.25-1.5mg/L) on the TCS decay. When the concentration of chlorine dioxide is high to low, the removal rates after the reaction time of 1 minute are about 99.8%, 99.75%, 99.69%, 99.52%, 99.1%, and 82.78%, respectively.

The reaction is most occurred in 20s. And the reaction rate is increasing as the concentration of chlorine dioxide increases. The removal rate of TCS by most different concentrations of chlorine dioxide has reached more than 95% in 30s. Only the chlorine dioxide at a concentration of 0.25 mg/L was only 82.78% in 1 minute.

3.4. Effect of initial concentration of TCS on TCS removal

The effect of the concentration of TCS on the co-existence to UV and chlorine dioxide was investigated at different concentrations (Figure 4).
The removal rate of the experimental TCS was almost 98%, and the removal rate of the TCS concentration of 500µg/L was 94%. This may be because the concentration of chlorine dioxide is insufficient, resulting in a decrease in the removal rate of TCS. Therefore, when the high concentration of pollutants is encountered in the actual use of UV and chlorine dioxide combined process, the concentration of chlorine dioxide can be appropriately increased.

3.5. Effect of humic acid on TCS removal
The effect of NOM was investigated with a commercial humic acid at different concentrations (Figure 5).

As can be seen from figure 5, when the humic acid reached the concentration of 9 mg/L, the removal rate of the chlorine dioxide and UV combined process was significantly reduced, and the removal rate was 95% after 20s. When the concentration of organic matter is lower than 7 mg/L, the removal rate of TCS is about 99%. Studies have shown that the presence of humic acid can inhibit the photolysis of TCS, and the inhibitory effect of humic acid is obvious [10]. Due to the inhibition of photolysis by humic acid, the effect of UV light is greatly reduced, which affects the overall removal rate. It shows that the organic matter in the solution will affect the removal efficiency of TCS by the combination of UV and chlorine dioxide, but the effect of low concentration of organic matter on the removal rate is limited.

3.6. Degradation products of TCS
In the experiment, the TCS degradation solution was subjected to solid-liquid extraction, and analyzed by GC/MS to determine the degradation products of TCS. In the experiment, we detected two degradation products, 2,4-DCP and 2,7-DCDD. Degradation product analysis results are shown in Figures 6, 7, and 8.
Figure 6. GC/MS chromatogram obtained by UV irradiation of TCS

It can be seen from Figure 6 that 10.9 min is the peak of 2,4-DCP, 31.78 min is the peak of 2,7-DCDD, and 33.89 min is the peak of TCS. The degradation products detected in the UV-degraded TCS solution were 2,4-DCP and 2,7-DCDD.

Figure 7. GC/MS chromatogram obtained by oxidation of TCS with ClO₂

It can be seen from Figure 7 that 10.9 min is the peak of 2,4-DCP, and 33.89 min is the peak of TCS. The degradation product detected by ClO₂ degradation in TCS solution was 2,4-DCP.

Figure 8. GC/MS chromatogram obtained by UV/ClO₂ degradation of TCS

The solution obtained by removing the TCS from UV/ClO₂ was subjected to solid-liquid extraction, and then subjected to GC/MS analysis. From Figure 8, it was found that 10.9 min was the peak of 2,4-DCP, and 33.89 min was the peak of TCS. The degradation product detected by UV/ClO₂ removal of TCS solution was 2,4-DCP, and 2,7-DCDD was not detected.
Comparing the above test results, the use of UV/ClO\textsubscript{2} to remove TCS can effectively reduce the formation of carcinogenic 2,7-DCDD.

4. Result
(1) UV/ClO\textsubscript{2}, ClO\textsubscript{2} and UV can remove TCS effectively, and the removal effect of TCS is: UV/ClO\textsubscript{2}>ClO\textsubscript{2}>UV.
(2) The removal efficiency increases as the pH increases. The removal rate within 1 minute of pH 5 was only 95.02%.
(3) The higher the concentration of humic acid, the smaller the removal rate of TCS.
(4) The higher the concentration of TCS, the lower the experimental removal effect. 2,4-DCP was generated during UV/ClO\textsubscript{2}, ClO\textsubscript{2} and UV, however, the production of 2,8-Cl\textsubscript{2}DD was not detected during UV/ClO\textsubscript{2} process.

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