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Triclosan photolysis: parameter investigation and photo-oxidation pathway

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Highlights

- TCS photo-oxidation investigation by parameter variation study and reaction mechanism.
- pH effect on TCS photodegradation.
- Photolysis enhancement by NO_3^-, HA and TiO_2.

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol; TCS), a broad-spectrum antimicrobial agent used as an active ingredient in skin and oral care consumer products, is becoming one of the most commonly detected organic pollutants in tap and superficial waters, due to its intensive and widespread use [1]. An effective technique for TCS removal from wastewaters has to be identified. UV light can degrade many of the commonly detected emerging pollutants at disinfection doses [2,3]. This paper deals with TCS photoremoval using a lab-scale experimental apparatus. The effect of Triclosan initial concentration (TCS_0), exposed solution volume (V), solution initial pH (pH), nitrate anions (NO_3^-) and humic acids (HA) as a function of the irradiation time (0-60 min), in order to study both direct photolysis and the combination of direct and indirect photolysis, were investigated. Furthermore, TCS heterogeneous catalytic photolysis was also studied by adding titanium dioxide powder (TiO_2) into experimental solutions. Eventually, a photo-oxidation by products were identified and a photoreaction mechanism was proposed.

2. Methods

Experimental solutions were prepared dissolving Triclosan powder in ultrapure water. The effect of parameter variation on Triclosan photolysis was investigated by adding sodium bicarbonate powder ($NaNO_3$), humic acids (HA) and titanium dioxide powder (TiO_2). The initial pH of the solutions was regulated by addition of NaOH or HCl. Experiments were carried out in a batch reactor of 100 mL (Petri dishes of 90 mm diameter) equipped with fixed UV light wavelength (UV_w) of 254 nm and at an irradiation intensity (E) of 400 mJ m^{-2} (Vilber-Lourmat BLX-254). The temperature was measured and kept constant at 20°C in all the experiments. Quantitative analyses were carried out using a Reverse Phase High Performance Liquid Chromatography technology (Shimadzu, Kyoto, Japan) performed with a Shimadzu DAD detector (SPD-M20A), equipped with Shimadzu LC-20AD. Experimental conditions investigated are summarized in Table 1. Investigations were performed in triplicate, however the average values are reported.

Run	Parameter Studied	Operating conditions (UV_w=254 nm; E=400 mJ m^{-2}; T=20 °C)
1	TCS_0=15.5-61.8 µM	V=100 mL; pH=6; NO_3^-=0 mg L^{-1}; HA=0 mg L^{-1}; TiO_2=0 mg L^{-1}
2	V= 25-100 mL	TCS_0=26.9 µM; pH=6; NO_3^-=0 mg L^{-1}; HA=0 mg L^{-1}; TiO_2=0 mg L^{-1}
3	pH=6; 10	V=100 mL; TCS_0=26.9 µM; NO_3^-=0 mg L^{-1}; HA=0 mg L^{-1}; TiO_2=0 mg L^{-1}
4	NO_3^-= 0-50 mg L^{-1}	V=100 mL; TCS_0=26.9 µM; ph=6[1]; HA=0 mg L^{-1}; TiO_2=0 mg L^{-1}
5	HA=10 mg L^{-1}	V=100 mL; TCS_0=26.9 µM; ph=6[1]; NO_3^-=0 mg L^{-1}; TiO_2=0 mg L^{-1}
6	TiO_2= 0-100 mg L^{-1}	V=100 mL; TCS_0=26.9 µM; ph=6[1]; NO_3^-=0 mg L^{-1}; HA=0 mg L^{-1}

Table 1. Experimental conditions.

3. Results and discussion

The effect of TCS_0, V, pH, NO_3^-, HA and TiO_2 on TCS photo-oxidation is shown in Figure 1. It is worth highlighting that, for all the conditions investigated, after an irradiation time of 15 minutes a TCS removal higher than 90% was observed. As shown, TCS removal seemed to not be significantly affected by TCS_0 (Fig. 1a)) and V (Fig. 1b)) while pH (Fig. 1c)), NO_3^- (Fig. 1d)), HA (Fig. 1e)) and TiO_2 (Fig. 1f)) seemed to be effective for TCS degradation. Two pH values were investigated: the former (pH = 6) lower while the latter (pH = 10) higher than pKa of Triclosan, equal to 8.1. Direct photolysis seemed to be mostly effective for TCS anionic species than for its molecular species, since TCS removal close to 99% and 95% for pH values of 10 and 6 were respectively found at an irradiation time lower than 30 minutes. pH experimental findings are consistent with literature data [4]. TCS removal was significantly enhanced by NO_3^-, HA and TiO_2, highlighting their role as photodegradation promoters, in agreement with literature findings [5,6].

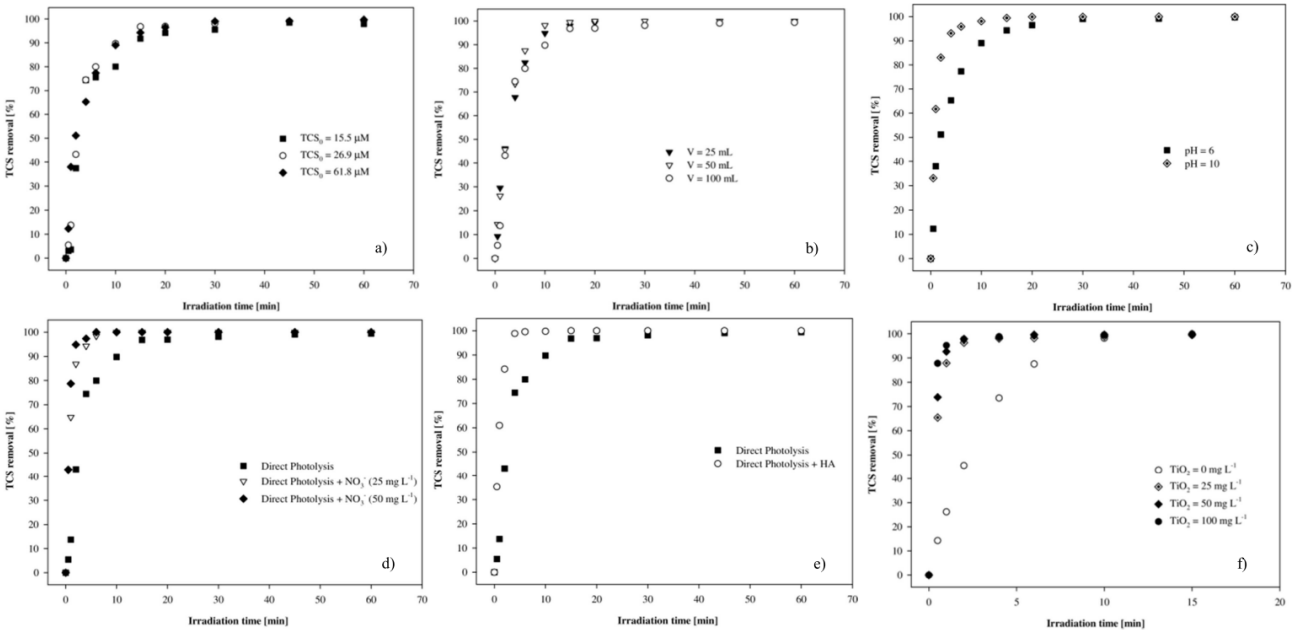

Figure 1. Effect of initial concentration of TCS (a), volume of the exposed solution (b), initial pH of the solution (c), nitrate anions (d), humic acids (e) and TiO_2 (f) on TCS photodegradation.

TCS photoreaction by-products were identified. Photodegradation mechanism was assumed as a series – parallel reaction system, with the TCS dissociation at equilibrium in the first step, while first-order photochemical reactions of the TCS molecular and anionic forms were considered as parallel reactions.

4. Conclusions

The effects of several parameters on TCS photodegradation were investigated in order to study direct photolysis, combination of direct and indirect photolysis and heterogeneous catalytic photodegradation. Promising TCS degradations were found for all the investigated experimental conditions. Eventually, photo-oxidation by-products were identified and a reaction mechanism was proposed.

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Keywords
Triclosan photolysis, photo-oxidation pathway, parameter investigation, kinetic modelling