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# Elimination of disinfection byproduct formation potential in reclaimed water during solar light irradiation



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### **ABSTRACT**

Ecological storage of reclaimed water in ponds and lakes is widely applied in water reuse. During reclaimed water storage, solar light can degrade pollutants and improve water quality. This study investigated the effects of solar light irradiation on the disinfection byproduct formation potential in reclaimed water, including haloacetonitriles (HANs), trichloronitromethane (TCNM), trihalomethanes (THMs), haloketones (HKs) and chloral hydrate (CH). Natural solar light significantly decreased the formation potential of HANs, TCNM, and HKs in reclaimed water, but had a limited effect on the formation potential of THMs and CH. Ultraviolet (UV) light in solar radiation played a dominant role in the decrease of the formation potential of HANs, TCNM and HKs. Among the disinfection byproducts, the removal kinetic constant of dichloroacetonitrile (DCAN) with irradiation dose was much larger than those for dichloropropanone (1,1-DCP), trichloropropanone (1,1,1-TCP) and TCNM. During solar irradiation, fluorescence spectra intensities of reclaimed water also decreased significantly. The removal of tyrosine (Tyr)-like and tryptophan (Trp)-like protein fluorescence spectra intensity volumes was correlated to the decrease in DCAN formation potential. Solar irradiation was demonstrated to degrade Trp, Tyr and their DCAN formation potential. The photolysis products of Trp after solar irradiation were detected as kynurenine and tryptamine, which had chloroform, CH and DCAN formation potential lower than those of Trp.

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## 1. Introduction

Wastewater reclamation and reuse is a practical method of providing an alternative water source to the public [\(Van and](#page--1-0) [Verbauwhede, 2004](#page--1-0)). To counteract the hourly and seasonal variations in demand for reclaimed water supply, water is usually stored in reservoirs, artificial lakes, rivers or ponds for later use ([Daniel, 1980\)](#page--1-0). During storage, organic matter in the reclaimed water is exposed to solar light, which has been shown to decrease ultraviolent absorbance and fluorescence intensity of dissolved organic matter in water [\(Chow et al., 2008; Lee and Hur, 2014; Wu](#page--1-0) [et al., 2016\)](#page--1-0). Because dissolved organic matter is known to act as an important precursor to disinfection byproducts (DBPs) during chlorination [\(Bond et al., 2011; Kim and Yu, 2005\)](#page--1-0), solar light may exert considerable effects on DBP formation of dissolved organic matter in water.

Studies have shown that solar light irradiation of surface water does not significantly change its trihalomethane (THM) formation potentials ([Chow et al., 2008](#page--1-0) and [2013](#page--1-0)), but that it decreases haloacetic acid (HAA) formation potential [\(Chow et al., 2008\)](#page--1-0) and increases the formation of chloral hydrate (CH) and haloacetonitriles (HANs) ([Chow et al., 2013](#page--1-0)). However, changes in DBP formation potential upon photodegradation vary with sources of organic matter [\(Lee and Hur, 2014\)](#page--1-0). Ultraviolet (UV) light irradiation of drinking water increases THM formation during subsequent

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chlorination [\(Dotson et al., 2010](#page--1-0)). Additionally, [Chu et al. \(2012\)](#page--1-0) found that UV irradiation at doses of  $19.5-585$  mJ/cm<sup>2</sup> reduced the formation potential of dichloroacetonitrile (DCAN) in tyrosine (Tyr) solution, a model precursor of HANs.

When compared with organic matter in drinking water, reclaimed water has high concentrations of such matter with complex components, and therefore exhibits strong formation potential of DBPs, especially nitrogenous ones (N-DBPs) ([Huang](#page--1-0) [et al., 2016; Templeton et al., 2010; Westerhoff and Mash, 2002\)](#page--1-0). HAN concentrations can reach 30 µg/L in reclaimed water [\(Krasner](#page--1-0) [et al., 2009\)](#page--1-0). Nitrogenous disinfection byproducts, including HANs and trichloronitromethane (TCNM), show greater cytotoxicity and genotoxicity than carbonous DBPs (C-DBPs) ([Plewa et al., 2008\)](#page--1-0), and have been of increasing concern. However, the effects of solar radiation on the formation potential of DBPs in reclaimed waters, especially N-DBPs, remain unknown.

Therefore, this study was conducted to examine changes in N-DBP and C-DBP formation potential in reclaimed water during solar light irradiation, and to evaluate the relationship between changes in DBP formation potentials and variations in fluorescence after irradiation. Mechanisms of DBP formation potential change in model fluorescent components were also investigated.

### 2. Materials and methods

### 2.1. Water samples

We used water samples from the effluents of two wastewater treatment plants (WWTP A and WWTP B) in Shenzhen, China. Samples A1 and A2 were obtained from the final effluent of WWTP A at two different times. Water sample B1 was taken from the UVdisinfection effluent of WWTP B. The main wastewater treatment processes were as follows.



Dissolved organic carbon (DOC), pH, and ammonia nitrogen concentrations were measured using a total organic carbon (TOC) analyzer (TOC-L, Shimadzu Corp., Kyoto, Japan), FE-20 detector (Mettler Toledo, Greifensee, Switzerland), and HI-96715 ammonia medium range analyzer (Hanna Instruments Inc., Woonsocket, RI, USA), respectively. The water quality parameters of the samples are shown in Table S1.

#### 2.2. Chemicals and materials

THMs (Supelco 47904), CH (47335-U) chemical standards, EPA 551B standard mixture (Supelco 48046) containing DCAN, trichloroacetonitrile, bromochloroacetonitrile, dibromoacetonitrile, dichloropropanone (1,1-DCP), trichloropropanone (1,1,1-TCP) and TCNM, Trp (purity 98%), kynurenine (Kyn, purity 95%), tryptamine (purity 98%), 1, 2-dibromopropane, methyl tert-butyl ether (MTBE, purity 99%) and sodium hypochlorite (NaOCl) were purchased from Sigma Aldrich (St. Louis, MO, USA.). Tyr with a purity of 98.9% was obtained from J&K Chemical (Shanghai, China).

#### 2.3. Light irradiation

Natural solar light irradiation of reclaimed water samples (30 mL) was performed in quartz glass tubes for 13 h at 22.9-27.5 °C during summer at 22°35N, 113°58E (Shenzhen, China). During simulated solar light irradiation, reclaimed water samples and the model chemicals, Trp and Tyr, in quartz glass tubes were exposed to a xenon lamp (1 KW) in a XPA-7 photochemical reactor (Xujiang Electromechanical Plant, China) for 13 h, with water sample temperatures 25.0  $\pm$  0.5 °C and pH values of 7.0  $\pm$  0.3 ([Wu et al., 2016\)](#page--1-0). To evaluate the effects of light wavelength on DBP formation potential, a xenon lamp with a UV light filter and a mercury lamp (300 W,  $\lambda_{\text{max}} = 375$  nm) were used to simulate visible ( $\lambda$  > 420 nm) and UV ( $\lambda$  < 400 nm) light, respectively. Given the limitation of the UV light filter we used, the minimum wavelength of simulated visible light used in this study was 420 nm instead of 400 nm. During irradiation, intensities of light with wavelengths of  $275-330$  nm,  $320-400$  nm, and  $400-1000$  nm were determined using UV-B, UV-A, and FZ-A irradiance meters, respectively (Beijing Normal University Photoelectric Instrument Factory, Beijing, China), after which the intensities of UV light  $( $400 \text{ nm}$ )$  and visible light  $(>400 \text{ nm})$  were calculated. The dark controls of reclaimed water samples in quartz glass tubes were kept without light irradiation at 25.0  $\pm$  0.5 °C. The excitation emission matrix of the fluorescence spectra of the water samples was determined using a fluorescence spectrophotometer (Hitachi F-7000; Hitachi, Tokyo, Japan) according to previously reported methods [\(Chen et al., 2003; Tang et al., 2014](#page--1-0)).

#### 2.4. Chlorination and DBP analyses

After solar irradiation, the samples were subjected to chlorination DBP formation potential tests. Chlorination experiments were conducted in 40 mL brown glass volumetric flasks with polytetrafluoroethylene lids [\(Huang et al., 2016](#page--1-0)). Disinfectant dosages for DBP formation potential tests for free chlorine were calculated by the equation proposed by Krasner et al.  $(2004)$ : Cl<sub>2</sub> dosage  $(mg)/$ L) =  $3 \times$  DOC (mg·C/L) +  $8 \times NH_3$  (mg·N/L) + 10 (mg/L). After the addition of free chlorine, the samples were chlorinated for 24 h at an ambient pH in a dark incubator at  $25$  °C. Thereafter, sodium thiosulfate (Na2S2O3) was applied as the dechlorination reagent at a dose about 1.5 times that of the chlorine dosage [\(http://www.](http://www.sciencedirect.com/science/article/pii/S0043135415302190) [sciencedirect.com/science/article/pii/S0043135415302190](http://www.sciencedirect.com/science/article/pii/S0043135415302190)[Farre](#page--1-0) [et al., 2013; Wang et al., 2014](#page--1-0); [http://www.sciencedirect.com/](http://www.sciencedirect.com/science/article/pii/S0043135415302190) [science/article/pii/S0043135415302190](http://www.sciencedirect.com/science/article/pii/S0043135415302190)[Yeh et al., 2014; Zhang](#page--1-0) [et al., 2015](#page--1-0)). To prevent decomposition of byproducts by the dechlorination reagent, samples were extracted immediately after quenching as described below.

The DBPs were extracted by liquid-liquid extraction into MTBE containing 1,2-dibromopropane as an internal standard in the presence of anhydrous sodium sulfate, then analyzed by gas chromatography (Agilent Technologies, Santa Clara, CA, USA) with an electron capture detector based on the United States Environmental Protection Agency (USEPA) method 551.1 [\(USEPA, 1995\)](#page--1-0). The detection limit of the DBPs was 0.1  $\mu$ g/L.

#### 2.5. Analysis of model chemicals and their photolysis products

The concentrations of Trp, Tyr and Kyn in solutions after simulated solar irradiation were determined by high-performance liquid chromatography with fluorescence and UV detectors (RF-20A and SPD-M20A; Shimadzu Corp) as previously described [\(Sa et al., 2011;](#page--1-0) [Vignau et al., 2004\)](#page--1-0). To determine the Trp and Tyr concentrations, an Atlantis C18 analytical column (Agela, 4.6 mm  $\times$  150 mm, 5 µm) was used. During analysis, the mobile phase was a mixture of Download English Version:

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