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Solar light irradiation significantly reduced cytotoxicity and disinfection byproducts in chlorinated reclaimed water

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ABSTRACT

Chlorinated reclaimed water is widely used for landscaping and recreational purposes, resulting in human exposure to toxic disinfection byproducts. Although the quality of chlorinated reclaimed water might be affected by sunlight during storage, the effects of solar light irradiation on the toxicity remain unknown. This study investigated the changes in cytotoxicity and total organic halogen (TOX) of chlorinated reclaimed water exposed to solar light. Irradiation with solar light for 12 h was found to significantly reduce the cytotoxicity of chlorinated reclaimed water by about 75%, with ultraviolet light being responsible for the majority of this reduction. Chlorine residual in reclaimed water tended to increase the cytotoxicity, and the synergy between solar light and free chlorine could not enhance the reduction of cytotoxicity. Adding hydroxyl radical scavengers revealed that the contribution of hydroxyl radical to cytotoxicity reduction was limited. Solar light irradiation concurrently reduced TOX. The low molecular weight (<1 kDa) fraction was the major contributor of cytotoxicity and TOX in chlorinated reclaimed water. Detoxification of the low molecular weight fraction by light irradiation was mainly a result of TOX dehalogenation, while detoxification of the high molecular weight (>1 kDa) fraction was probably caused by photoconversion from high toxic TOX to low toxic TOX.

1. Introduction

Reclamation of wastewater is an essential way to alleviate the growing water shortage. During many urban applications of reclaimed water, such as garden irrigation, car washing, scenic water replenishment, it is possible to expose humans to reclaimed water and pollutants through inhalation, dermal absorption, and ingestion (Xue et al., 2016). Owing to the various chemical pollutants and pathogenic microorganisms it contains, the safety of reclaimed water must be taken into good consideration (Li et al., 2017a). Chlorination is widely used to inactivate pathogens during the treatment of reclaimed water (Zhang et al., 2016), but the reaction of disinfectants and dissolved organic matter (DOM) leads to formation of disinfection byproducts (DBPs) (Sadiq and Rodriguez, 2004; Du et al., 2017a). Many regulated DBPs are genotoxic and carcinogenic and could therefore have adverse effects on humans (Richardson et al., 2007).

Assessments of individual DBPs can only provide limited information on chlorinated reclaimed water because of the complexity of DBP mixture. More than 600 DBPs have been identified over the past decades, but only a small part of them underwent systematic toxicology assessments (Richardson et al., 2007; Dong et al., 2016). Besides, the combined effect of different DBPs on toxicity is also difficult to determine. Moreover, the potential risk of DBP mixture is greater in reclaimed water than that in drinking water because of the complex composition and characteristics of DOM (Hu et al., 2016). Instead, bioassays are considered effective and

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straightforward for measuring the toxicity of chlorinated effluents (Watson et al., 2012). Biotoxicity tests conducted on microbes, such as luminescent bacteria and *D. manga*, are developed earlier and are relatively complete, but they are less effective at predicting the human health risk (Plewa et al., 2000). Alternatively, measurement of cytotoxicity against mammalian cells provides a convenient and ideal tool for risk determination (Plewa et al., 2004). Also, recent works have demonstrated that the comprehensive toxicity was positively correlated to the total organic halogen (TOX) of chlorinated water (Gong et al., 2016; Pan et al., 2013; Zhu and Zhang, 2016). Therefore, investigating the toxicity and TOX of chlorinated reclaimed water is of great importance.

After being discharged into a receiving aquatic environment, the reclaimed water quality could be affected by many factors. Contaminants carried with reclaimed water (such as DBPs) can be transported and converted via sorption, hydrolysis, biodegradation, volatilization and photolysis (Chen et al., 2008). Photolysis of some DBPs under sunlight irradiation have been reported. Nitrosamines were found to be rapidly photodegraded, while chloroform, dichloroacetamide, and chloral hydrate were generally stable (Chen et al., 2010; Abusallout and Hua, 2016a). Although mixtures of DBPs were also found to decrease in response to solar light irradiation (Abusallout and Hua, 2016b; Liu et al., 2017), the effects of solar light irradiation on toxicity of chlorinated effluent are still unknown.

The free chlorine in receiving water can be degraded by UV light and produce free radicals (Watts and Linden, 2007). Solar/chlorine or UV/chlorine synergistic effects have been confirmed to be more efficient at degradation of various contaminants than UV irradiation or chlorination alone (Qin et al., 2014; Wang et al., 2016; Sun et al., 2016). While in some studies, the enhanced DBPs formation during the UV/chlorine treatment process raised concern. During the degradation of ibuprofen by UV/chlorine, a significant increase in total organic chlorine (TOCl) was observed, while it was negligible during dark chlorination (Xiang et al., 2016). In addition to the higher formation of adsorbable organic chlorine (AOCl), Wang et al. (2017) found that the cytotoxicity generated during UV/chlorine treatment of carbamazepine was also higher than that of chlorination alone. However, the effects of combined solar light and free chlorine on DBP mixtures have not been thoroughly investigated, and the changes in cytotoxicity remain unknown.

Therefore, this study investigated the variations in cytotoxicity and TOX of chlorinated reclaimed water during exposure to simulated solar light. The effects of light wavelength, free chlorine and hydroxyl radicals on the reduction of toxicity were determined, and changes in the cytotoxicity and TOX in different molecular weight fractions were analyzed.

2. Materials and methods

2.1. Water sampling and analysis

Water samples S1, S2 and S3 were obtained at different times from the outlet of a wastewater treatment plant (WWTP) that employs an aerobic-anoxic-oxic process in southern China. The samples were transferred to the laboratory on ice to maintain the temperature of 2–6 °C, and all the subsequent analysis and chlorination were performed within 24 h.

Before undergoing the water quality analyses, all samples were passed through glass membranes with 0.45 μm pores (Whatmman, UK). The pH values were measured with a glass electrode (PB-10, Sartorius Design, Germany). The dissolved organic carbon (DOC) concentrations were measured with a total organic carbon analyzer (TOC-L; Shimadzu, Japan). The ultraviolet absorbance (UV_{254}) was measured using a UV-2600 spectrophotometer (Shimadzu, Japan). The bromide concentration was measured with an ion chromatograph (IC2010; Tosoh, Japan). The results of the water quality analyses are shown in Table S1.

2.2. Chlorination

The filtered water samples were chlorinated with NaClO at 15 mg/L (expressed as Cl_2 concentration) in glass bottles for 1 h. The pH of the water samples was adjusted to 7.0 ± 0.1 by H_2SO_4 or NaOH and stabilized with phosphate buffer prior to chlorination.

To determine the synergistic effects of chlorine residual and solar light on cytotoxicity changes, the chlorine dosage was adjusted to make there was no chlorine residual in water samples after 1 h chlorination. And then, extra NaClO was added into experimental group after chlorination to give 10 or 30 mg/L free chlorine right before light exposure, while control group underwent simulated solar light irradiation without extra NaClO added.

2.3. Separation of different molecular weight fractions by ultrafiltration

To determine variations in different molecular weight (MW) fractions during irradiation, the chlorinated water samples (1 L) were separated with an ultrafiltration membrane (1 kDa; Millipore, USA) using a stirred ultrafiltration cell (8400, Millipore, USA). The membrane was installed in the cell and was washed with ultrapure water until the DOC of the effluent was <0.1 mg/L before use. Next, the sample was poured into the cell and filtered following the manufacturer's instructions. When there was 50 mL sample left, filtration was stopped and the cell was filled with new sample. This process was repeated until 1 L of sample was filtered. The collected effluent (950 mL) was the <1 kDa fraction, and the 50 mL sample remaining in the cell was the >1 kDa fraction. To remove the lower molecular weight fraction as completely as possible, 300 mL ultrapure water was added to the cell, mixed with the 50 mL sample, and then filtered until there was 50 mL left in the cell. This operation was repeated three times, after which the finally acquired 50 mL > 1 kDa fraction was diluted to 1 L to obtain the original concentration.

2.4. Irradiation experiments with simulated solar light

The irradiation experiments were conducted according to Wu et al. (2016a). Briefly, water samples (chlorinated and unchlorinated) were stored in quartz cups (500 mL) and exposed to simulated solar light (1 kW xenon lamp; Xujiang Electromechanical Plant, China; the spectrum was shown in Fig. S1) for 24 h, 12 h or 6 h in different experiments. Quartz cups were then placed around the lamp with a visible light intensity of 60 mW/cm^2 and UV light intensity of 1 mW/cm^2 received during experiments. Intensities of light with wavelengths of 275–330 nm, 320–400 nm, and 400–1000 nm were measured using UV-B, UV-A, and FZ-A irradiance meters, respectively (Beijing Normal University Photoelectric Instrument Factory, Beijing, China), and the intensities of UV light and visible light were calculated. During irradiation, the pH and temperature of water samples were maintained at 7.0 ± 0.1 and 25.0 ± 0.5 °C, respectively.

Water samples were exposed to visible light ($\lambda > 420$ nm) and UV light ($275 < \lambda < 420$ nm) to determine the effects of light wavelength on the reduction of cytotoxicity. The visible light was acquired by filtration of a xenon lamp with a UV light filter, and the UV light was provided by a mercury lamp (300 W, $\lambda_{max} = 375$ nm). The intensity of UV light was 2.6 mW/cm^2.

To determine the effects of hydroxyl radicals (·OH) on the reduction of cytotoxicity during irradiation, tert butyl alcohol (TBA;