Investigation of ozonation kinetics and transformation products of sucralose

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HIGHLIGHTS

- Ozonation of sucralose was initiated by the formation of ·OH radical.
- Sucralose could be completely degraded by ozone at basic and neutral conditions in the excess ozone.
- Rate constants of sucralose ozonation could be significantly inhibited by TBA, carbonate and humic acid.
- Carboxylic acids, aldehydes and probable chloride containing products could be generated during sucralose ozonation.
- A ozone degradation pathway of sucralose was proposed, which might be different from those ·OH generated from UV.

GRAPHICAL ABSTRACT
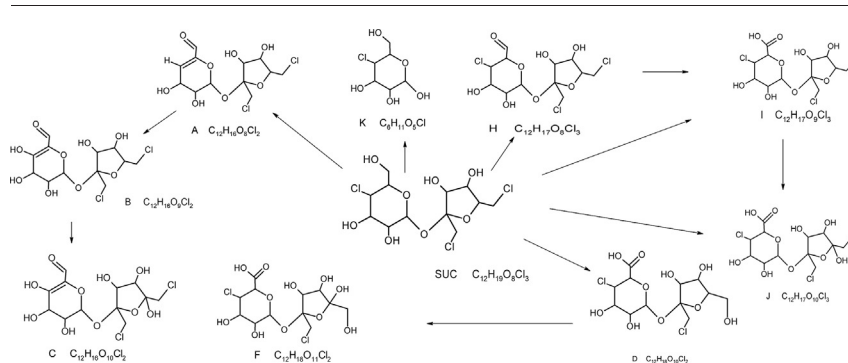
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ABSTRACT

Sucralose is one of widely used artificial sweeteners, which has been ubiquitously detected in various water sources, such as wastewater and randomly in reservoir water. It is also reported to be persistent to various water treatment techniques. Although there are some studies on removal of sucralose by advanced oxidation process, limited information, in terms of reaction kinetics, transformation products and degradation pathway etc., was reported in its ozonation process. In this study, the reaction kinetics, removal efficiency, influence of pH, humic acid and carbonate on sucralose degradation by ozone, have been studied systematically. The results demonstrated that ozonation of sucralose was initiated by the formation of •OH radical. Sucralose could be completely removed with excess O_3 at neutral and basic conditions in ultrapure water. The rate of degradation decreased significantly in acidic condition and in the presence of carbonate and •OH radical scavenger (e.g. tert-butanol). The acidity was the key factor affecting the degradation of sucralose. The rate constant was about 500 times higher at pH 7 than that at pH 4. Transformation products study indicated that the ozonation of sucralose were more complex than that in photolysis reaction. Although ozonation of sucralose was initiated by •OH radical, both •OH radical and O_3 might be involved in the formation of transformation products and total organic carbon (TOC) removal. Various transformation products, such as aldehydes, carboxylic acids and probable chloride containing products, were identified and characterized in details. An ozonation degradation pathway of sucralose was proposed as well.

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1. Introduction

Artificial sweeteners are used as food additives as they provide a sweet taste to food but have few calories, thus they are also known as non-nutritive sweeteners (NNS) (FDA, 2006). Seven artificial sweeteners, such as sucralose (SUC), saccharin, aspartame, acesulfame potassium, neotame, stevia, and Luo Han Guo extract etc., are approved by the U.S. Food and Drug Administration (FDA) (Pepino et al., 2013).

Sucralose is about 600 times sweeter by weight than sucrose, which has been widely used in over 80 countries and in >4000 different products (Sharma et al., 2012; Torres et al., 2011). There are about 1500 ton and 400 ton sucralose consumed every year in USA and Europe, respectively (Sharma et al., 2014).

Sucralose is very stable with a half-life of several years (Scheurer et al., 2009). It is also stable in human body, there is >98% consumed SUC unchanged in human excretion (Lange et al., 2012). Various studies showed that SUC was persistent to environment and water treatment processes (Pasquini et al., 2013). For example, there was only 20% of SUC converted to CO_2 in 14 days with the rate of 1.43 ng SUC/kg per day in a 0.1 μg SUC/kg of soil (Labare and Alexander, 1994). There was no significant degradation of SUC in aerobic or anaerobic biological reactors after 42–62 days; and there was only 7.8% of SUC degraded with UV light irradiation up to 24 h. At free chlorine concentration (0.1 mM), which is normally applied in the wastewater treatment plants (WWTPs), there was only 1.5% of SUC degraded in 96 h, while 79% of SUC could be degraded when the free chlorine concentration was increased to 100 mM (Torres et al., 2011). Furthermore, as the octanol-water partition coefficient (log·K_{ow}) of SUC is 0.3, SUC will be present in aqueous phase and is less bioaccumulated (Tollefsen et al., 2012; Hoque et al., 2014). Therefore, SUC may accumulate in natural waters over time due to its increased consumption, and persistence to water treatment (Lubick, 2008). In US, sucralose was detected in source water of 15 out of 19 drinking water treatment plant (DWTPs) at the concentration level of 47 ng·L^{-1}–2900 ng·L^{-1}, finished water of 13 out of 17 DWTPs at the concentration level of 49 ng·L^{-1}–2400 ng·L^{-1} and distribution system water of 8 out of 12 DWTPs at the concentration level of 48 ng·L^{-1}–2400 ng·L^{-1} in US (Mawhinney et al., 2011). SUC was detected in all samples of septic tank effluent and all groundwater samples in the concentration range of 6–98 μg·L^{-1} and 0.7–77 μg·L^{-1}, respectively, in Canada (Robertson et al., 2016). In Germany, 2.7 μg·L^{-1} SUC was detected in wastewater effluent (Oppenheimer et al., 2011), and SUC were detected in the range of 2.2–9.1 μg·L^{-1} in the influent and effluent of WWTP of Zurich (Switzerland) (Buerge et al., 2009). Thus, SUC was recommended as an ideal chemical marker of domestic wastewater in groundwater (Oppenheimer et al., 2011; Buerge et al., 2009; De Sousa et al., 2014). SUC was used as one of chemical markers in the human fecal pollution source tracking toolbox (Tran et al., 2015).

Although SUC is generally recognized as safe for use, the concerns of long-term impacts of sucralose to the human health and environment have attracted many research interests due to its stability in environment, persistence to treatment processes, potential accumulation in aquatic environment and widely applications. It was reported that the SUC could interfere with plant photosynthesis and change organisms' feeding behaviors (Lubick, 2008). Based on Ecological Structure Activity Relationship Model (ECOSAR) developed by USEPA, when the concentration was higher than 1123 mg·L^{-1} (chronic lowest no effect concentration of green algae), SUC may cause toxicity to aquatic organisms (Tollefsen et al., 2012; USEPA, 2010). By oral gavage of splenda (containing 1.1% of sucralose) from 100–1000 mg·kg^{-1} to male Sprague-Dawley rats for 12-wk., the study by Abou-Donia et al. also showed a decrease in gastrointestinal microflora and an increase in expression of cytochrome P450 and P-glycoprotein (Abou-Donia et al., 2008). However, no adverse effects were observed in green algae, Lemna gibba, with 1800 mg·L^{-1} of SUC for 96 h (Smyth, 1986), and Lemna gibba with concentration of 114 mg·L^{-1} for 7 days (Lillicrap, 2011). Compared with SUC concentrations detected in the various environments as discussed above, these concentrations are too high to be environmentally relevant. There was no observed toxicity in Nitocra spinipes for 96 h exposure at concentrations of 10 mg·L^{-1} (Wiklund et al., 2012). The toxic effect of Cd^{2+} and Cu^{2+} to S. obliquus decreased with the presence of 1 mg L^{-1} of SUC, while impacts of SUC to the growth of S. obliquus was not significant (Hu et al., 2016a).

In the last few years, there were only few studies have been conducted on the SUC ozonation in water. Hollender et al. (2009) reported that only about 31% of SUC could be eliminated with 0.6 g O_3 g^{-1} DOC. Scheurer et al. (2010) reported that SUC was persistent during ozonation, with removal of 8–15% in waterworks and <20% after 30 min in the batch test. Torres et al. (2011) reported that estimate the rate constant of $k = 4.5 \times 10^{-3} \pm 1 \times 10^{-3}$ M^{-1} s^{-1} of SUC ozonation in the presence of both O_3 and •OH as oxidants at pH 7.2. Study of Soh et al. (2011) showed that the initial first order reaction rate of SUC ozonation was 0.00427 s^{-1}. In these studies, only Soh et al. (2011) reported that 6% of 0.39 mg·L^{-1} sucralose could be removed by 4.8 mg·L^{-1} ozone after 1 h. The degradation of sucralose by ozone was completely hindered in the addition of 0.5 mM t-butanol (TBA) as a radical quench, suggested a radical mediated oxidation. However, the rate constant was determined only at around neutral condition and only the effect of TBA on the SUC ozonation was studied. Other parameters such as humic acid (HA), carbonate, and pH were no studied in details. Therefore, there is need to conducted more details kinetics studies on the SUC ozonation.

Further studies on the toxicity and environment impacts of SUC and its transformation products (TPs) showed that the inhibition of the luminescence of Vibrio fischeri which was exposed to photocatalytic irradiated sucralose sample (15 mg·L^{-1}) increased in the first 1 h and decreased after 2 h (Calza et al., 2013). At pH 3, only <1% of sucralose was hydrolyzed to 1, 6- dichloro-1,6-dideoxy-D-fructose (1,6-DCF) and 4-chloro-4-deoxy- D-galactose (4-CG) in one year at 25 °C (Grice and Goldsmith, 2000; Labare and Alexander, 1994). Thermal degradation products polychlorinated aromatic hydrocarbons and chloropropanols were observed when temperature was higher than 120 °C (De Oliveira et al., 2015; Rahn and Yaylayan, 2010). Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) were detected in smoke and residues generated from heated SUC, and the presence of CuO enhanced the formation of PCDD/PCDF in comparison with Al_2O_3 and Fe_2O_3 (Dong et al., 2013). For SUC samples treated with UV/H_2O_2, two products with m/z of 361, 379 and 381 were detected (Keen and Linden, 2013). Similarly, various $[Na]^+$ adduct of SUC photocatalytic degradation products, e.g. m/z $C_{12}H_{19}O_9Cl_3Na$, $C_{12}H_{19}O_{10}Cl_3Na$ and $C_{12}H_{22}O_{10}Na$ etc. were also reported by Calza et al. (2013). However, there is no ozonation products of SUC reported. The effects of these TPs, formed during water treatment process, on the environment and human health are still not very clear.

The objective of this study is to investigate the kinetics of SUC ozonation, the effect of pH and water matrix on the removal of SUC by O_3, ozonation TPs and the possible ozonation pathways via the application of modern analytical techniques, so as to provide qualitative and quantitative information on ozonation of sucralose in water.

2. Experiments

2.1. Chemicals, reagents and materials

SUC, acetonitrile (ACN), methanol (MeOH), formic acid (FA), acetic acid (AA), oxalic acid (OXA) and sodium thiosulfate, sodium carbonate and humid acid were purchased from Sigma-Aldrich Co. Deionized (DI) water was obtained by passing tap water through a Milli-Q integral 5 system (Millipore, Singapore) with a resistivity >18.2 M·Ω·cm^{-1} and an on-line TOC <5 μg·L^{-1}. Stock solution of SUC, FA, AA and OXA were prepared in DI water at 1000 mg·L^{-1} and further diluted to the calibration level in DI water for quantitation. Humic acid stock solution was prepared by dissolving 2 g of humic acid in 1 L of DI water at pH 10