Chemical Engineering Journal 353 (2018) 626–634

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Performance of artificial sweetener sucralose mineralization via UV/O_3 process: Kinetics, toxicity and intermediates

Yin Xu[a], Ying Wu[a], Wei Zhang[a], Xiaohui Fan[a], Yan Wang[a,b,*], Hui Zhang[a,*]

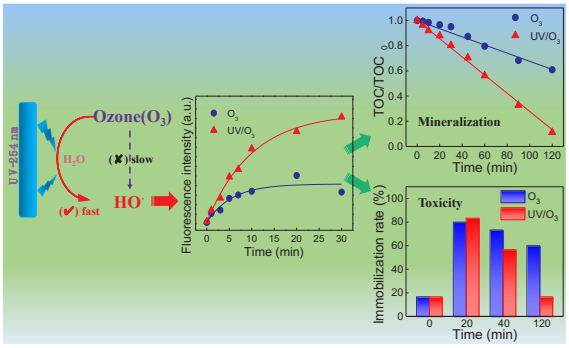
[a] Department of Environmental Science and Engineering, Hubei Environmental Remediation Material Engineering Technology Research Center, Wuhan University, Wuhan 430079, China

[b] Department of Environmental Science and Engineering, Anhui Science and Technology University, Donghua Road 9#, Fengyang 233100, China

HIGHLIGHTS

- UV/O_3 can efficiently degrade the emerging contaminant sucralose (SUC).
- Effect of primary parameters on the SUC mineralization were investigated.
- Mineralization rate of SUC was affected by common anions (Cl^- and NO_3^-).
- Toxicity evaluation verify the detoxification effect of UV/O_3 process.
- A mineralization pathway was proposed based on the identified by-products.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Sucralose (SUC)
UV/O_3 process
Kinetics
Mineralization
Transformation products

ABSTRACT

Sucralose (SUC) is ubiquitously present in aquatic ecosystems in many parts of the world, owing to its widespread usage and ineffective elimination in wastewater treatment plants. This study investigated the mineralization of SUC in aqueous solution via UV/O_3 process and found that SUC can be mineralized efficiently. Effect of several operating parameters like solution pH, O_3 concentration, gas flow rate and initial SUC concentration, on TOC removal were explored. Results indicated that the mineralization efficiency of SUC reached almost 90% in 120 min after UV/O_3 treatment at neutral pH. The intensity of hydroxyl radicals generated in sole O_3 and UV/O_3 processes were compared using the fluorescence spectra analysis. Toxicity tests carried out using *Daphnia Magna* indicated that the UV/O_3 process under the used experimental conditions was much more effective in the detoxification of the SUC solution than sole O_3 process. The presence of inorganic anion like NO_3^- exhibited an enhancement on the mineralization rate, while Cl^- showed some positive effect at low concentration (1 mM) but inhibited SUC mineralization at higher concentrations (10–200 mM). Finally, the intermediates produced in UV/O_3 process were identified by LC-MS analysis and a possible transformation pathway was briefly discussed.

1. Introduction

Sucralose (SUC) is a chlorinated carbohydrate that has been widely used as a substitute of sugar in the past two decades [1], due to the approval by the Federal Drug Administration of United States in 1998 [2]. As one of non-nutritive artificial sweeteners, today SUC has been found globally for use in thousands of products and is consumed by billions of people annually. Now it has overtaken traditional saccharine

* Corresponding authors at: Department of Environmental Science and Engineering, Wuhan University, Wuhan 430079, China (H. Zhang).
E-mail addresses: wangyanht@163.com (Y. Wang), eeng@whu.edu.cn (H. Zhang).

https://doi.org/10.1016/j.cej.2018.07.090
Received 24 February 2018; Received in revised form 25 June 2018; Accepted 12 July 2018
Available online 30 July 2018
1385-8947/

and aspartame as the most popular commercial sweetener [3], and it is estimated that the consumption of SUC will increase in recent years. Despite its widespread use, the safety of SUC has remained controversial due to its potential impact on metabolism, body weight, and energy homeostasis [4–6].

SUC is not easily metabolized in the human body or other animals; instead, it travels through the digestive system and is excreted through urine and feces, before finally reaches municipal wastewater treatment plants (WWTPs) [3,7]. SUC is very stable and not efficiently removed or transformed in WWTPs. Conventional and advanced wastewater treatment processes (e.g. biodegradation, river bank filtration, flocculation, chlorination, UV disinfection and direct ozone oxidation) have been reported to be ineffective for the SUC elimination [3,8]. After entering the environment, SUC is also unaffected by the common environmental contaminant degradation processes such as microbial degradation and photolysis. For instance, SUC did not show any degradation in aerobic or anaerobic biological reactors even after 62 days of treatment [9]. The half-lives up to 4 months were observed in the biodegradation of SUC in soil [10]. Consequently, SUC has been found to occur at ng L^{-1} to mg L^{-1} levels in wastewaters [11,12], suspended particulate matter of wastewater [13], river and coastal waters [14,15], ground waters [16], landfill leachates [17], sewage sludge [10,18], and even in drinking water [19]. Owing to it widespread occurrence and persistence, sucralose has been flagged as an emerging contaminant by the U.S. Environmental Protection Agency (USEPA) [20]. At present there are few concerns about SUC effects on aquatic life based on its low bioconcentration factor. However, constant input of SUC into the natural waters and remarkable persistence of the compound may result in its accumulation in ecology environment beyond the concentration at which no adverse environmental effects are observed [3]. Therefore, the study of effective alternative treatment approaches in WWTPs for SUC removal is required.

In recent decades, ozonation is a widely applied technology for the removal of various organic micropollutants in water. Furthermore, ozonation has been intensively tested as an advanced wastewater treatment technology in laboratory-, pilot- and full-scale studies [21]. However, SUC was proved to be recalcitrant to ozonation and some studies have reported the ineffectiveness of ozone for the transformation of SUC in water [8,9]. For example, Scheurer et al. [8] reported that its removal efficiency was less than 20% in the laboratory test and waterworks, though a depletion of about 30% for SUC was achieved with 5 mg L^{-1} ozone. This is in agreement with another work, which showed only 31 ± 6% sucralose likely to be removed in a water treatment plant upgraded with ozonation [22]. Torres et al. [9] reported that part of SUC was removed after 96 h contact with ozone, and the oxidation rate constant was estimated to be approximately $4.5 \pm 1 \times 10^{-3}\ M^{-1}\ s^{-1}$ based on SUC ozonation experiments at pH 7.2. Similar result was also found by Soh et al. [23], who indicated that the initial first order rate constant of SUC by ozonation was 0.00427 s^{-1}.

Usually organic compounds can be oxidized through direct reaction with ozone, and also via radical mediated oxidation. SUC does not appear to have evident sites of attack by molecular ozone, and the degradation of SUC was hypothesized to be due to the hydroxyl radicals ($HO^{\cdot}$) generated in the oxidative process [7,23,24]. To overcome the disadvantage of selectivity and low reaction rate of sole ozonation, ozone can be combined with some techniques such as ultraviolet (UV) radiation. Then ozone can be converted into $HO^{\cdot}$, which is the most reactive radical and is capable of unselectively reacting with almost all types of organics in water. As a promising technology for elimination of emerging pollutants [25], UV/O_3 process with the generation of a large amount of $HO^{\cdot}$ has shown to be an available option. This combination can not only increase the O_3 utilization rate but also enhance the mineralization of pollutants. However, no report about SUC degradation by UV/O_3 process has been found in the literature, though several studies have investigated SUC degradation using hydroxyl or sulfate radical based advanced oxidation processes [26–29].

The primary objectives of this study are: (i) to investigate the mineralization of SUC under various operational conditions in aqueous solution, specifically, pH, O_3 concentration, gas flow rate (Q), initial SUC concentration, and common anions (Cl^- and NO_3^-); (ii) to compare the production of $HO^{\cdot}$ between O_3 and UV/O_3 processes using fluorescence spectra analysis with coumarin being employed as a chemical probe, and to assess the detoxification efficiency of the O_3 and UV/O_3 process using *Daphnia Magna* acute immobilization tests; (iii) to identify the transformation products in the early stage of SUC degradation by UV/O_3 process using LC-MS and to reveal the possible degradation pathway of SUC.

2. Materials and methods

2.1. Chemicals

Sucralose ($C_{12}H_{19}Cl_3O_8$, purity 98%) was obtained from Aladdin Industrial Corporation (Shanghai, China). Coumarin ($C_9H_6O_2$, reagent grade), sodium chloride (NaCl, analytical grade) and sodium nitrate ($NaNO_3$, analytical grade) used in this experiments were purchased from Sinopharm Chemical Reagent Co., Ltd. China. All chemicals were used without further purification. All stock solutions were freshly prepared in Milli-Q supplied by water purification system (UPK, Ulupure).

2.2. Experimental procedure

The SUC degradation experiments were performed in a cylindrical glass reactor containing 250 mL SUC solution (Fig. S1). The dimensions of jacketed reactor are 80 mm (external diameter) × 300 mm (external height) and 40 mm (inner diameter) × 285 mm (inner height), respectively. The length and diameter of UV lamp (TUV6W/G6T5, 254 nm, Philips) are 226.3 mm and 16.0 mm, respectively. The SUC solution was exposed to a UV lamp which was placed vertically in the center of the reactor. The radiation strength of the UV light source was determined to be 33.4 W m^{-2} in average using potassium peroxodisulphate chemical actinometry [30]. Except otherwise specified, the initial SUC concentration was fixed at 50 mg L^{-1} (equivalent to 18.11 mg L^{-1} of TOC) and the reaction pH was maintained at 7.0 using 50.0 mM phosphate buffer solutions. A magnetic stirrer (RW 20, IKA) fixed at 450 revolutions per minute (rpm) was utilized to homogenize the solutions. Ozone was produced by an ozone generator (XFZ-5BI, Tsinghua Tonghui) with electric discharge using the dried oxygen with purity of 99.9%. The bubbling of ozone gas into the solution was started, and at the same time the UV light was switched on. At specific time intervals, samples were withdrawn by syringe and analyzed immediately after 1 mL $Na_2S_2O_3$ solution (1.0 M) was added to quench any residual oxidizing species. Cooling water was pumped circularly to maintain the reaction temperature constant at 25 °C, the increase in temperature due to UV irradiation was less than 2 °C.

2.3. Analytical methods

Ozone concentrations in the gas phase $[O_3]_g$ was monitored by iodometric method with potassium iodide solution [31]. Total organic carbon (TOC) was determined by an Analytik Jena analyzer with quantification limit of 4.0 μg L^{-1} (Multi N/C 3100, Analytik Jena). Coumarin (1 mM) was used as a chemical probe for hydroxyl radical formation. The concentration in 7-hydroxycoumarin, product of the reaction between coumarin and $HO^{\cdot}$, was determined by measuring the fluorescence emission at 452 nm under excitation at 332 nm using a spectrofluorometer (F-4500 FL Spectrophotometer, Shimadzu).

The acute toxicity of the reaction solution before and after treatment was evaluated by *D. magna* immobilization essays [32,33]. *D. magna* organism was cultivated more than three offsprings in the laboratory. Before the tests, aeration was added into the samples to