



Oxidative transformation of artificial sweetener acesulfame by permanganate: Reaction kinetics, transformation products and pathways, and ecotoxicity



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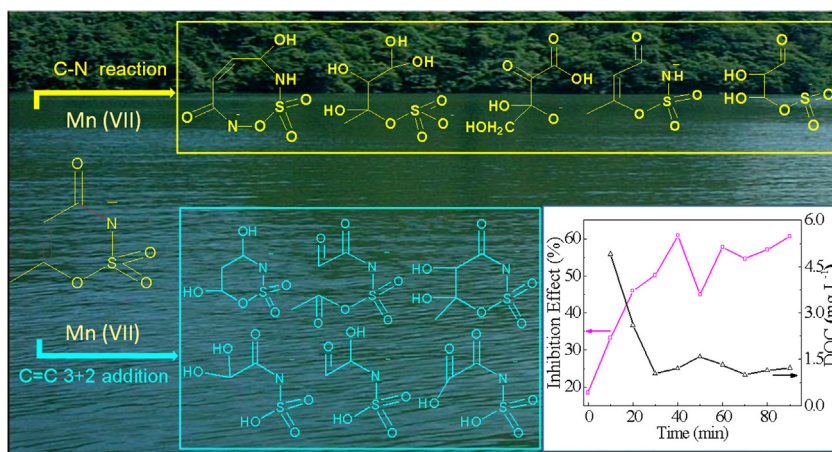
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HIGHLIGHTS

- Transformation pathways of acesulfame oxidation with Mn(VII) were proposed.
- New transformation products on acesulfame oxidation were identified.
- Environmentally relevant conditions were systematically investigated.
- Ecotoxicity of transformation products of acesulfame oxidation was evaluated.
- Acesulfame oxidation with Mn(VII) in real water was studied.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 September 2016

Received in revised form 2 December 2016

Accepted 8 February 2017

Keywords:

Acesulfame
Permanganate oxidant
Transformation product
Transformation pathway
Ecotoxicity

ABSTRACT

Acesulfame has attracted much attention due to its wide application, environmental persistence and potential safety risk of transformation products (TPs). Little information is known on acesulfame transformation in the presence of oxidants/disinfectants. The acesulfame oxidation by permanganate (Mn(VII)) in water under environmentally relevant conditions was systematically evaluated. The pH of water showed negligible influence in acesulfame oxidation. Inorganic ligand (pyrophosphate) exhibited insignificant effect whereas organic ligands (oxalate, ethylene diamine tetraacetic acid, and humic acid) exerted obvious suppression on acesulfame oxidation. Natural organic matter in real water had important influence in acesulfame oxidation by Mn(VII). Acesulfame transformation pathways were initiated by the attack of Mn(VII) on double bond of ring via [3 + 2] addition electrocyclic reaction and rich electron of N moiety through electrophilic reaction, followed by oxidation and hydrolysis reactions to produce TPs. Among them, five TPs were for the first time identified. The ecotoxicity tests uncover higher toxicity of the TPs than acesulfame itself. The study on oxidative transformation of acesulfame by Mn(VII) would illumine

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comprehensive evaluation of this emerging contaminant. Water treatment plants need to consider cautiously to protect the safety of downstream system when using Mn(VII) to dispose the water resource containing acesulfame or other artificial sweeteners.

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1. Introduction

Acesulfame is principally and widely used as artificial sweetener in the food additives and beverage [1]. The released artificial sweeteners have led to its ubiquitous occurrence in environment [2–4]. Levels of artificial sweeteners especially acesulfame are often above $1 \mu\text{g L}^{-1}$ in surface waters, which is much higher than most emerging contaminants. For example, acesulfame concentrations in the effluents of municipal wastewater treatment plants (WWTPs) in Gossau and Wädenswil were reported to be as high as $46 \mu\text{g L}^{-1}$ [5], and even average effluent concentration was reported up to $76.1 \mu\text{g L}^{-1}$ in Europe [6]. Previous studies have shown that acesulfame is exceedingly resistant to degradation by microorganism from WWTPs [7] and to hydrolysis under natural environmental condition [8], which render the constant accumulation of acesulfame in the aquatic environment. Realities must be envisaged that its possible environmental effect including ecotoxicity and fate is cause for concern.

Acesulfame can be transformed in the presence of natural sunlight and microorganism [8], contributing to the natural attenuation of this important anthropogenic contaminant. This means that joint effect of photolysis and biodegradation might be potentially utilized for treatment of acesulfame-containing water area or remediation of acesulfame-impacted environmental matrices. Ozone (O_3) has been shown to be effective to control of acesulfame contamination and elucidate the main oxidation products containing acetic acid and an aldehyde hydrate [9]. Radical-based advanced oxidation process (AOP) treatments for artificial sweeteners could be feasible only after natural organic matter (NOM) was removed in advance [10]. Transformation of acesulfame by UV/TiO₂ revealed that more persistent byproducts were >500 times more toxic than acesulfame itself [11]. Artificial sweeteners are engineered as metabolically inert sugar substitutes. However, these artificial sweeteners including acesulfame have recently been recognized as a group of emerging environmental contaminants [12–14]. It is therefore crucial to evaluate the efficacy of water treatment methods employed and/or exploit new techniques to effectively remove acesulfame from contaminated water.

To date, little information is known on the transformation of acesulfame in the presence of common oxidants/disinfectants at the drinking water plants (DWP) and WWTPs, except for O_3 [9] and UV-based [15,16]. Various studies have indicated that these oxidants are preferentially effective in disposing emerging organic contaminant containing electron-rich moieties [17,18]. Among them, Mn(VII) has received much more attention as a green chemical oxidant due to its venerable characteristic of ease of handling, relatively low cost, comparative stability over a wide of pH range, as well as non-halogenated property [19]. Mn(VII) is a strong oxidizing agent that has been already widely used for in situ chemical oxidation (ISCO) in remediating contaminated soil, groundwater and surface water [20–22]. Simultaneously, it also has been widely used by water utilities to control dissolved manganese, taste/odor/color, and biological growth [23,24]. In particular, Mn(VII) has been demonstrated to be fairly effective in treating flame retardants [25–27], antibiotics [28,29] and endocrine-disrupting chemicals (EDCs) [18,30]. The oxidative transformation of artificial sweet-

eners, especially acesulfame by Mn(VII) has not been previously reported.

In this study, the oxidative transformation of acesulfame by Mn(VII) was studied. The reaction kinetics were investigated in a wide pH range of 4–9, where the effects of Mn(VII) concentration, temperature and ligands were surveyed. The transformation products (TPs) were identified by HPLC-ESI-tqMS combined with LTQ Orbitrap Velos Pro and the reaction pathways were proposed. The toxicity of TPs in mixture was assessed by bioluminescent microtox test using the marine bacterium *Vibrio fischeri*. Further, the effectiveness of Mn(VII) for decomposing acesulfame in real water was examined.

2. Experiment section

2.1. Materials

Acesulfame K (purity >98%) was purchased from Tokyo Chemical Industry Development Co., Ltd. (China). Potassium permanganate (Mn(VII)) was purchased Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). High-performance liquid chromatography (HPLC)-grade methanol was from Honeywell Burdick & Jackson (Ulsan, Korea). HPLC-grade ammonium acetate was obtained from Anqua Chemicals Supply. Mn(VII) stock solution was prepared by dissolving Mn(VII) in Milli-Q water. Unless otherwise stated, other reagents were analytical grade.

2.2. Oxidation in synthetic buffered waters

Kinetic reactions were launched by addition of excess Mn(VII) into solutions including acesulfame and other interesting constituents. The pH of reaction solution was regulated using acetate-acetic acid buffer (10 mM) for pH 4–6 and borate-boric acid buffer (10 mM) for pH 7–9. No distinct change of pH values (<0.1 unit) measured at the end of kinetic runs was observed. Unlike phosphate buffers, acetate and borate buffers have negligible influence on Mn(VII) reactions [30]. The reaction temperatures were adjusted by water bath. Samples were periodically collected, quenched with hydroxylamine, and then filtered with $0.22 \mu\text{m}$ nitrocellulose filter before analysis.

2.3. Oxidation in real waters

Influent water and tertiary effluent water were taken from Hunan Liantai wastewater treatment plant. Other real water samples were obtained in Xiangjiang River and Taozi Lake, respectively. After filtration through $0.45 \mu\text{m}$ nitrocellulose, samples were stored at 4°C and used within 72 h.

2.4. Analytical methods

A HITACHI L-2130 HPLC equipped with an Inert Sustain C18 column ($4.6 \times 250 \text{ mm}$, $5 \mu\text{m}$ particle size) and L-2420 UV-vis detector was used to quantify the acesulfame concentration according previous reported method [3] with certain modifications to achieve a rapid analysis. The isocratic mobile phase was consisted of 10% methanol and 90% 0.02 M ammonium acetate solution at a flow rate of 1 mL min^{-1} , the column temperature was hold at 35°C .

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