



Study on the kinetics and transformation products of salicylic acid in water via ozonation



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HIGHLIGHTS

- An integrated ozonation transformation products of salicylic acid were characterized.
- Kinetic and mechanism of salicylic acid were depended on the pH, ozone dose and the presence of natural organic matters.
- New compounds, acrylic acid, was identified as ozonation transformation product of salicylic acid.
- The ozonation pathways of salicylic acid in water sample were proposed and explained at acidic and basic conditions.

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ABSTRACT

As salicylic acid is one of widely used pharmaceuticals, its residue has been found in various environmental water systems e.g. wastewater, surface water, treated water and drinking water. It has been reported that salicylic acid can be efficiently removed by advanced oxidation processes, but there are few studies on its transformation products and ozonation mechanisms during ozonation process. The objective of this study is to characterize the transformation products, investigate the degradation mechanisms at different pH, and propose the ozonation pathways of salicylic acid. The results showed that the rate of degradation was about 10 times higher at acidic condition than that at alkaline condition in the first 1 min when 1 mg L⁻¹ of ozone solution was added into 1 mg L⁻¹ of salicylic acid solution. It was proposed that ozone direct oxidation mechanism dominates at acidic condition, while indirect •OH radical mechanism dominates at alkaline condition. A two stages pseudo-first order reaction was proposed at different pH conditions. Various hydroxylation products, carbonyl compounds and carboxylic acids, such as 2,5-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, catechol, formaldehyde, glyoxal, acetaldehyde, maleic acid, acetic acid and oxalic acid etc. were identified as ozonation transformation products. In addition, acrylic acid was identified, for the first time, as ozonation transformation products through high resolution liquid chromatography-time of flight mass spectrometer. The information demonstrated in this study will help us to better understand the possible effects of ozonation products on the water quality. The degradation pathways of salicylic acid by ozonation in water sample were proposed. As both O₃ and •OH radical were important in the reactions, the degradation pathways of salicylic acid by ozonation in water sample were proposed at acidic and basic conditions. To our knowledge, there was no integrated study reported on the ozonation of salicylic acid in water, in terms of transformation products, kinetic, mechanism, as well as degradation pathways.

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1. Introduction

In the past ten years, ozone based advanced oxidation processes (AOP), such as O₃, O₃/H₂O₂, O₃/UV, have been demonstrated to be a promising technology in disinfection of microorganisms, eliminating inorganic and organic pollutants, as well as controlling taste

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and odor problems etc. (USEPA, 1999; Glaze et al., 1987; Crittenden et al., 2012; Gottschalk et al., 2010). At post-ozonation process, the removal efficiencies were more than 85% for many compounds (e.g. azithromycin, ketoprofen, trimethoprim, propranolol etc.), with an ozone dose at 0.6 g O₃/g dissolved organic carbon (DOC) (Hollender et al., 2009). However, it was found that some compounds were resistant to ozone, such as iopamidol, sucralose, atrazine-desethyl etc., with the removal efficiency only at 10%–30% (Hollender et al., 2009). High concentration of ozone was needed for wastewater. For example, the rate of removal were from 50%–70% for acidic and neutral pharmaceutical products (e.g. salicylic acid, ibuprofen, triclosan, carbamazepine and diclofenac etc.) at an ozone concentration of 10 mg L⁻¹, while it would increase to 85%–95% at a concentration of 20 mg L⁻¹ (Gagnon et al., 2008). To enhance the removal efficiency and reduce ozone dosage, some combination ozone processes, such as ozone/hydrogen peroxide, ozone with sand filtration and GAC filtration etc., have been used to remove ozone resistant contaminants, e.g. more than 80% geosmin and 2-methylisoborneol (2-MIB) can be effectively removed by O₃/H₂O₂ or ozone/sand filtration/GAC filtration (Ferguson et al., 1990, 1991).

Compared with chlorination, the advantage of ozonation is that it does not produce chlorinated trihalomethanes (THMs), haloacetic acids (HAAs) or other chlorinated products. However, ozone can react with nature organic matters (NOM), and produce a variety of oxidation transformation products, such as, aldehydes, ketones, and carboxylic acids, and peroxides etc. Bromide-containing water treated by ozone forms brominated products, bromate (BrO₃), which is a human carcinogenic compound (Siddiqui et al., 1995). Chlorination of ozonated drinking water results in increased levels of chloral hydrate as a result of the chlorination of acetaldehyde. Subsequently, chloral hydrate may be degraded to chloroform (LeBe and Benoit, 2000).

Salicylic acid (SA) is a phenolic phytohormone compound with bacteriostatic, fungicidal, and keratolytic actions. It has been widely used to treat many skin disorders, e.g. acne, dandruff, seborrheic, scalp, calluses and corns etc. There are up to 40% of SA present in salicylic acid plaster, 6% in shampoo etc. (NIH, 2012; Prugen, 2013). The presence of SA in the environmental water systems can be produced from industrial waste (e.g. olive oil distillation industries, chemical and pharmaceutical industries), household wastes, pharmaceutical residues, metabolite of acetylsalicylic acid (ASA) and by plants. ASA is used as a non-steroidal anti-inflammatory drug. It was reported that there are about 40,000 tonnes of acetylsalicylic acid (ASA) consumed each year (Warner and Mitchell, 2002). As it can be degraded to salicylic acid *in vivo*, ASA is one of the main medical sources of SA.

In the past years, SA had been detected at various levels in the environmental water systems. In groundwater, SA was found at the concentration range of 43 ng L⁻¹–1,225 ng L⁻¹, with an average concentration of 418 ng L⁻¹ (Lapworth et al., 2012). SA was even detected in certain tap water at contraction range of 16.6 ng L⁻¹–41.2 ng L⁻¹. In the latest study, SA were detected in 17 of 22 river water samples at an average concentration of 70 ng L⁻¹, all 22 river sediments samples at an average concentration of 318 ng L⁻¹, all 11 mineral water at an average concentration of 33 ng L⁻¹, all 21 wastewater treatment plants (WWTPs) influent samples at a concentration of 295 ng L⁻¹ and all 21 WWTPs effluent samples with an average concentration of 30 ng L⁻¹ (Carmona et al., 2014). Up to 13 µg L⁻¹ of SA was detected in sewage effluents in Greece and Spain (Heberer, 2002). And 96,000–253,000 ng kg⁻¹ of SA was detected in biosolids (Daughton and Ruhoy, 2009).

Various studies on the degradation of salicylic acid by different treatment processes have been reported. Grootveld and Halliwell

(1986) found that salicylate metabolites 2,5 -dihydroxybenzoate, 2,3-dihydroxybenzoate and catechol with the relative amounts of ~40%, ~49% and ~11% respectively in the biological samples, collected from patients with long-term aspirin treatment. Pulse radiolysis study showed that salicylate reacted with •OH at a rate constant of 5×10^{-9} – 10^{-10} M⁻¹ s⁻¹ (Hiller and Wilson, 1983; Moorhouse et al., 1985). In the study by Albarranm and Schuler (2003), •OH radicals were produced at a rate of ~10 µMmin⁻¹, with the presence of 2.5–10 mM ferricyanide and saturated with N₂O, radiolysis products, such as catechol, 2,5-dihydroxybenzoic acid (2,5-DHBA), 2,6-dihydroxybenzoic acid (2,6-DHBA), 2,3-dihydroxybenzoic acid (2,3-DHBA) and 2,4-dihydroxybenzoic acid (2,4-DHBA), were detected by liquid chromatographic (LC) and capillary electrophoretic (CE), coupled with diode array detector (DAD) at wavelength from 200 to 400 nm. In another study by Parisheva & Nusheva, the degree of degradation of SA by •OH radicals was increased from 55%–91%, and the COD reduction was increased from 8% to 40% in 30–40 min, when the pH was increased from 6 to 10. Oxalic acid was identified as a major intermediate by UV/vis spectrophotometer (Parisheva and Nusheva, 2007) with initial SA concentration of 200 mg L⁻¹, which was much higher than that presence in the environmental water system (16.6 ng L⁻¹–13 µg L⁻¹, as discussed in the previous section), by 40 min reaction with continuous bubbling of ozone gas (Parisheva and Nusheva, 2007).

There was about 99.6% of SA that can be degraded by combination of UV/O₃/H₂O₂ in 40 min, while 3 h was need to achieve 87% of degradation with H₂O₂/COD = 5 at an initial pH of 7 (Mandavgane and Yenki, 2011). Karnik et al. (2007) used salicylic acid as a model compound to investigate hydroxyl radical reaction in an ozonation-coated/uncoated membrane filtration hybrid process at pH 2.5–3.0 and pH 7.9–8.1. The study showed that there were no transformation product detected in the treated water from either ozonation or membrane filtration alone at pH of 2.5–3, only two compounds, 2,3-DHBA and 2,5-DHBA were identified by GC-MS at pH of 8.

Interestingly, these studies have shown different products on the ozonation or hydroxylation of salicylic acid, possibly due to different experiments conditions, different reaction mechanisms under different studies, or limits of detection approaches, which attract us to conduct an integrated study on the ozonation of salicylic acid. The objective of this study is to investigate the effect of pH on the formation of transformation products, kinetics of salicylic acid removal and possible reaction pathways by ozonation via the application of modern analytical techniques, so as to provide qualitative and quantitative information on the ozonation of salicylic acid in water. An integrated ozonation transformation products study will not only characterize molecules directly degraded from parent SA molecule but also small molecules, like carbonyl compounds and carboxylic acids etc.

2. Material and methods

2.1. Chemicals and reagents

Salicylic acid, catechol, 2,5-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, acetonitrile, methanol, benzyl bromide, *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA), acetone, 2-butaone, muconic acid, fumaric acid, maleic acid, acrylic acid, *tert*-butyl alcohol (t-BuOH, TBA), formic acid (FA), acetic acid (AA), oxalic acid (OXA) and sodium thiosulfate were purchased from Sigma-Aldrich Co. Carbonyl compounds Mix A (13 compounds, 1.0 mg mL⁻¹ in acetonitrile) & carbonyl compounds Mix B (2 compounds, 1.0 mg mL⁻¹ in acetonitrile) were purchased from AccuStandard Inc. (125 Market Street, New Haven, CT 06513, USA).

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