



The removal efficiency and degradation pathway of IPMP and IBMP in aqueous solution during ozonization



Chaoyi Wang, Chongwei Li, Haipu Li*, Hsiaowan Lee, Zhaoguang Yang*

Center for Environment and Water Resources, College of Chemistry & Chemical Engineering, Central South University, No. 932 Lushan Road, Yuelu District, Changsha 410083, PR China

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ABSTRACT

2-isopropyl-3-methoxy pyrazine (IPMP) and 2-isobutyl-3-methoxy pyrazine (IBMP) are two of main taste and odor compounds in drinking water. The removal efficiency and possible degradation pathway of IPMP and IBMP by ozonization were studied by evaluating experimental parameters including ozonization time, initial concentration of IPMP and IBMP, and solution pH. At pH 6.8 the removal efficiency of IPMP and IBMP (100 ng L^{-1}) were both found over 90% within 15 min ozonization, and a higher pH value (8.6) helped to accelerate the degradation in some degree. In both neutral and acidic media, the degradation followed the pseudo first order kinetics. In contrast, at lower pH range, e.g. pH 5.0, more than 10% of the title compounds were still existing even after 30 min ozonization. With increasing the initial concentration from 100 to 200 and to 400 ng L^{-1} , the removal efficiency of the title compounds was decreased successively. The intermediate by-products of IPMP and IBMP by ozonization were mainly acid esters and carboxylic acids as identified by GC-MS, and accordingly the possible degradation pathway was proposed.

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1. Introduction

Taste and odor (T&O) compounds in drinking water have attracted considerable public and governmental attention, and become an important issue for customers to evaluate the water quality [1–3]. In recent years, 2-isopropyl-3-methoxy pyrazine (IPMP) and 2-isobutyl-3-methoxy pyrazine (IBMP), the two of main T&O compounds causing a rotten vegetable odor, had been frequently found in freshwater lakes, such as Taihu Lake, Gehu Lake, and Nanyang Lake in China, and Lake Greifensee, Lake Zurich, and Lake Lucerne in Swiss, with concentrations ranging from 10 to 65 ng L^{-1} [4–6]. Various solutions to remove T&O compounds in aqueous solution were developed, for example, by simple adsorption with activated carbon or through advanced oxidation processes (AOPs) with UV, H_2O_2 or O_3 . On the other hand, some researches focused on the degradation kinetics [7,8], pathway, and by-products [9–11] of odor compounds to deepen the understanding of the degradation process [12].

An et al. studied the adsorption of IPMP and IBMP at the initial concentration of $750 \text{ } \mu\text{g L}^{-1}$ using granular activated carbon [13]. Antonopoulou et al. explored the TiO_2 photocatalysis of IPMP

(10 mg L^{-1}) concerning kinetics, degradation pathways and toxicity evaluation [14]. Peter et al. reported the oxidation kinetic of IPMP ($0.5 \text{ } \mu\text{M}$) by ozonization, and found the rate constant of IPMP is hundreds of times more than those of geosmin and 2-methylisobomeol (MIB) under the same condition [8]. In addition, catalytic ozonization of IPMP ($38 \text{ } \mu\text{g L}^{-1}$) by $\gamma\text{-AlOOH}$ and $\gamma\text{-Al}_2\text{O}_3$ has been reported in laboratory research [15]. In the process of water treatment plants (WTPs), however, catalysts were not yet well practiced in ozonization to decompose IPMP and IBMP [16–19].

Among these techniques, ozonization has been widely used in WTPs [20] and is highly related to our research interests. As known, the odor threshold concentrations of IPMP and IBMP are as low as 0.2 and 1 ng L^{-1} , respectively [8,20–22]. It is also noticeable that in the most reports the initial concentrations of these two T&O compounds were at the level of $\mu\text{g L}^{-1}$ or mg L^{-1} , which are too high for the real water samples. Thus research on the initial concentration at ng L^{-1} level is calling for a comprehensive investigation [23].

It is also necessary to examine the formation of by-products during ozonization, because some of them may generate fragrant or stinking smell or pose a risk to human health. Qi et al. found that the major intermediate by-products of IPMP in catalytic ozonization by $\gamma\text{-AlOOH}$ were aliphatic amines [15]. Antonopoulou et al. explored the photo-induced transformation of IPMP and proved

* Corresponding authors.

E-mail addresses: lihaipu@csu.edu.cn (H. Li), zgyang3@gmail.com (Z. Yang).

the formation of intermediate products via hydroxylation, oxidation and demethylation pathways [14].

In the current study, ozonization of IPMP and IBMP at hundreds ng L^{-1} level were investigated under different conditions by varying parameters including degradation time, initial concentration of T&O compounds, and solution pH. Furthermore, the possible degradation pathway of IPMP and IBMP by ozonization was studied using gas chromatography-mass spectrometer (GC-MS) to explore the reaction mechanism.

2. Materials and methods

2.1. Materials

IPMP and IBMP were purchased from Sigma-Aldrich (USA) as solutions of $100 \mu\text{g mL}^{-1}$ in methanol. IPMP and IBMP were diluted with methanol of pesticide residue (PR) grade, which was purchased from Aladdin. Ozone was produced by a corona discharge ozone generator (XLK-G 20, XiangLu Environment Protection Technology Co. Ltd., Changsha, China) supplied with air. NaCl (AR) was dried off in Muffle furnace at 450°C for 4 h. The silylation kit (N,O-bis(trimethylsilyl) trifluoroacetamide + trimethylchlorosilane (BSTFA + TMCS), 99:1) was from Supelco, Bellefonte, PA, USA. Other materials were of analytical or guarantee reagent grade.

2.2. Ozonization

Ozonization was carried out in a glass reaction flask (250 mL) with 100 mL synthetic water containing IPMP and IBMP. Ozone was produced by the ozone generator constantly and flowed through a T-cock before bubbled into the bottom of the reactor through a thin tube. The flow rate of ozone was determined as $0.4938 \text{ mg min}^{-1}$ using the back titration of potassium iodide with standardized sodium thiosulfate [24,25]. The residual ozone was absorbed by 0.1 mol L^{-1} sodium thiosulfate solution. Samples were taken when the reactions had run at intervals of 5 min until 30 min. These samples were analyzed with GC-MS. All ozonization experiments were run at ambient temperatures of $25 \pm 1^\circ\text{C}$ at designed pH. Each experiment was made triplicate for average.

2.3. Analytical methods

2.3.1. Quantitative analysis of IPMP and IBMP

IPMP and IBMP in aqueous solution were extracted using headspace-solid phase microextraction (HS-SPME), and were detected

with GC-MS [26]. In the HS-SPME procedure, 8 mL water sample was placed into a 15 mL vial containing a magnetic stirrer. After adding of 2.5 g NaCl, the vial was sealed with a silicon-Teflon septum cap. The sealed vial was preheated for 10 min at 60°C , followed by 30 min HS-SPME under the same temperature, with a stirring rate of 500 rpm. SPME apparatus, including a $65 \mu\text{m}$ polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber, was penetrated the septum and the fiber was extended into the headspace for extraction. After extraction, the fiber was immediately inserted into the GC injection port for desorption.

The GC injection temperature was set at 250°C in the splitless mode and the fiber was desorbed for 5 min. The analysis was measured with an Agilent 7890 series GC system coupled with a 5975C series mass spectral detector. The carrier gas was high purity helium (99.9999%) with a constant flow rate of 1 mL min^{-1} . The oven temperature was programmed from an initial temperature of 50°C held for 3 min, then ramped to 90°C at $15^\circ\text{C min}^{-1}$, finally ramped to 150°C at 5°C min^{-1} and held for 1 min. The total programming time was 19.667 min. The GC-MS transfer line temperature was 200°C . The electron impact (EI) ion source temperature was 230°C and the quadrupole temperature was 150°C . The EI ionization mode was at electron energy of 70 eV, with the m/z ranging from 40 to 170 amu to determine appropriate masses for selected ion monitoring (SIM). Mass spectral quantitative ions were m/z 124, 137 and 152 for IPMP and m/z 124 and 151 for IBMP, respectively.

2.3.2. Qualitative analysis of by-products by ozonization of IPMP and IBMP

As ozone is a strong oxidant [27], ozonization of IPMP and IBMP in water may be nonselective and the degradation by-products could be in volatile, semi-volatile or nonvolatile forms. Thus, three extraction methods, SPME, liquid-liquid extraction and silanization were respectively taken to extract these by-products for being detected by GC-MS. The analysis process was illustrated in Fig. 1.

In each experiment with the initial concentration of $10 \mu\text{g L}^{-1}$, samples (each 16 mL) were taken at 0.5, 1, 2, 3, 5, 10, 15, 20 and 30 min intervals.

Each sample was split into two equal parts; one part was extracted by SPME under the same condition described in Section 2.3.1 and the other was extracted manually with 5 mL of ethyl acetate (AR). As for the latter, after shaking for around 2 min, 1 mL of extracted phase was analyzed with GC-MS, and the rest of extract phase was placed into a 4 mL vial. The ethyl acetate solution was dried with N_2 ($\geq 99.999\%$) at the room temperature. After

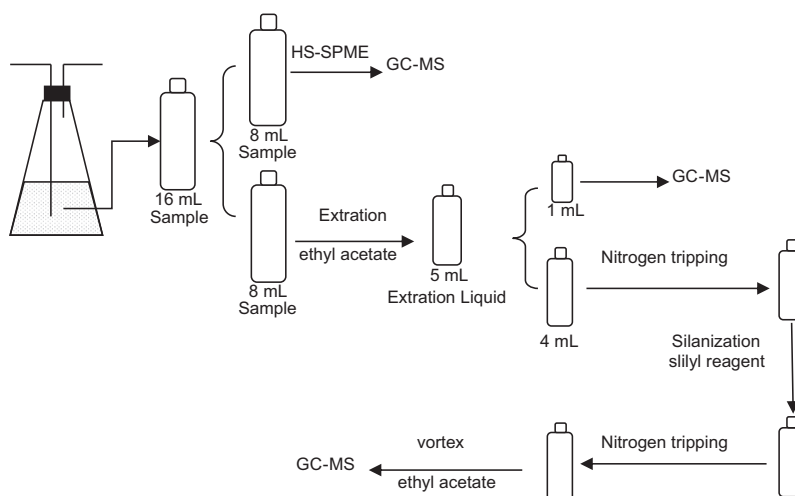


Fig. 1. Analysis of degradation by-products of IPMP and IBMP by ozonization.

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