Kinetics and mechanism for omethoate degradation by catalytic ozonation with Fe(III)-loaded activated carbon in water

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HIGHLIGHTS

- ▶ The second-order rate constants of OMT reacting with O_3 and $\cdot OH$ were determined.
- ▶ OMT was predominantly degraded by $\cdot OH$ in catalytic ozonation with Fe@AC.
- ▶ Byproducts were identified to propose the pathways of OMT degradation.
- ▶ The toxicity of OMT solution decreased gradually during catalytic ozonation.

GRAPHICAL ABSTRACT

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ABSTRACT

The kinetics and mechanism for degradation of omethoate (OMT) by catalytic ozonation with Fe(III)-loaded activated carbon (Fe@AC) were investigated in this study with focus on identification of degradation byproducts. The rate constants of OMT reacting with ozone and hydroxyl radical ($\cdot OH$) were determined to be 0.04 and $5.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7.5 and 20°C , respectively. OMT was predominantly degraded by $\cdot OH$ in the catalytic ozonation with Fe@AC. The high-molecular-weight degradation byproducts identified were *O,O,O*-trimethyl phosphoric ester (TMP), pyrrolidin-2-one, *N*-methyl-2-(methylthio)acetamide, 2-(methylthio)acetamide, *O,O,S*-trimethylthiophosphate (STMP), and *N*-methyl-2-(methylthio)acetamide. Besides, low-molecular-weight organic acids and inorganic anions were also detected and quantified, including formic, acetic and oxalic acids as well as nitrate, sulfate and phosphate ions. In the catalytic ozonation, TMP and phosphate were two major P-containing byproducts resulting from OMT degradation. The toxicity of OMT solution gradually decreased during the catalytic ozonation, indicating that Fe@AC is a safe catalyst for OMT removal by ozone in water.

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1. Introduction

Organophosphorus pesticides (OPPs) are commonly used to control pests on cotton, rice, sorghum, sugarcane and vegetables, generally acting as cholinesterase inhibitors (Wu et al., 2009).

However, OPPs have a high acute toxicity to animals and humans. Omethoate (OMT) is a typical OPP used most widely in developing countries, whose production in China amounted to 8679 tons in 2005. Since a number of highly toxic pesticides have been prohibited in many countries in recent years (e.g., acephatemet and parathion-methyl), there will be an even larger demand for OMT.

OMT can enter into natural waters after its agricultural utilization and thus leads to micro-pollution of drinking water sources (Coupe et al., 2000; Schipper et al., 2008). Due to its high

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hydrophilicity ($K_{ow} = -0.74$) and low biodegradability, OMT has been frequently detected in many rivers and coastal waters (Li et al., 2005; Wang et al., 2007). The existence of OMT in water, even at a low concentration, will pose a potential threat to human health considering its high toxicity. However, conventional drinking water treatment processes, such as coagulation, sedimentation and filtration, are of low efficiency in removing OMT from water.

Ozone has been reported to be capable of removing many OPPs from water effectively (Meijers et al., 1995; Kim et al., 2002); however, oxidative byproducts will emerge in water instead, being still harmful to humans. Even worse, many of these byproducts are more toxic than their parent forms (Wu et al., 2009). For example, dimethoate could be oxidized to OMT, which is about 10 times as toxic as dimethoate. Similarly, the oxidative byproduct paraoxon is much more toxic than parathion. This is because the P=O bond in oxidative byproducts can directly combine with acetylcholinesterase in mammal bodies to yield toxic effects, while the P=S bond in parent compounds has to be transformed to the P=O bond first through metabolism or oxidation. In particular, the degradation byproducts of OPPs formed during ozonation have attracted the attention of many researchers. Dichlorvos was found to be reactive with ozone, but its oxidative byproducts were still toxic and difficult to degrade by ozonation alone (Kim et al., 2002). During the ozonation of alachlor, many byproducts were detected, while the toxicity of alachlor solution was only reduced slightly (Qiang et al., 2010).

Our previous work has indicated that catalytic ozonation with Fe(III)-loaded activated carbon (Fe@AC) could remove OMT effectively (Ling et al., 2011). Comparing with ozonation alone, the OMT removal was significantly enhanced in the O_3 /Fe@AC process through effective generation of hydroxyl radicals ($\cdot OH$), especially in the pH range of 7.0–8.0. The degradation of OMT was mainly attributed to $\cdot OH$ oxidation in the catalytic ozonation. However, the oxidative transformation of OMT in this process remains largely unknown.

The objectives of this study were to determine the rate constants of OMT reacting with ozone and $\cdot OH$, identify degradation byproducts so as to establish possible reaction pathways, and evaluate the toxicity change of OMT solution during the reaction course.

2. Materials and methods

2.1. Chemicals and catalyst

OMT (98%) and *O,O,S*-trimethylthiophosphate (STMP, 97%) were purchased from Dr. Ehrenstorfer, and *O,O,O*-trimethyl phosphoric ester (TMP, 98%) was from Acros. Sodium salts of formate, acetate and oxalate, and *para*-chlorobenzoic acid (*p*CBA) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Sodium sulfate, nitrate and phosphate were purchased from Tianjin Institute of Jingke Fine Chemicals. Other reagents were at least of analytical grade and used without further purification. All aqueous solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA).

Fe@AC used in catalytic ozonation was prepared according to the method developed previously (Ling et al., 2011). In brief, activated carbon particles with diameters of 100–200 μm were immersed in a ferric nitrate solution. The suspension was shaken at 20 °C for 24 h, and cured in oven at 105 °C for 12 h. The prepared Fe@AC particles were sieved and those of 100–200 μm were used in experiments.

2.2. Analytical methods

Aqueous ozone concentration was monitored by the indigo method (Bader and Hoigné, 1982). OMT was analyzed according

to our previous work (Ling et al., 2011). The concentration of *p*CBA was measured with high-performance liquid chromatography (HPLC, Agilent 1200) at 234 nm, which was coupled with a diode array detector (DAD) and an Atlantis dC18 column (4.6 $\times$ 250 mm, Waters). A mixture of 10 mM H_3PO_4 and methanol (3:7, v/v) was used as eluent at a flow rate of 1 mL min⁻¹.

Solid-phase extraction (SPE) was applied with the 500-mg HLB extraction cartridges (Waters) prior to the analysis of TMP and STMP. The HLB cartridge was conditioned with 10 mL methanol and 10 mL H_2SO_4 solution (pH 2.0) in sequence. After passage of 100 mL reaction sample, the cartridge was dried and then eluted with 10 mL mixture of dichloromethane and methanol (8:2, v/v). The extract was dried under a gentle stream of nitrogen gas and then re-dissolved with 1 mL acetone. Afterwards, TMP and STMP were analyzed by gas chromatography/mass spectrometry (GC/MS, Agilent 7890 GC and 5975 MSD) coupled with an HP-5 MS column (30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness). Helium gas was used as carrier gas at a flow rate of 1 mL min⁻¹. The front inlet temperature was 300 °C. The oven temperature started at 40 °C and held for 2 min, ramped linearly to 100 °C at 3 °C min⁻¹ and held for 5 min, and further increased to 290 °C at 20 °C min⁻¹. The MSD was operated in the electron ionization mode at 70 eV. For quantitative analysis, the selective ion mode was adopted with a quantification ion of m/z 110 for TMP and m/z 156 for STMP.

Low-molecular-weight (LMW) organic acids and inorganic anions were quantified by ion chromatography (IC, Dionex 2000) with an Ionpac AS19-HC 4 mm column. For LMW organic acids, the following elution gradient was used: started with 3 mM KOH and held for 20 min, increased to 15 mM KOH over 0.1 min and held for 20 min, decreased to 3 mM KOH over 0.1 min and held for 5 min. The retention times of formate, acetate and oxalate were 10.9, 12.9 and 37.0 min, respectively. For inorganic anions, the elution gradient was as follows: started with 10 mM KOH and held for 25 min, increased to 30 mM KOH over 0.1 min and held for 15 min, decreased to 10 mM KOH over 0.1 min and held for 5 min. The retention times of nitrate, sulfate and phosphate were 13.8, 28.7 and 39.0 min, respectively.

2.3. Determination of reaction rate constants

The rate constant of an organic compound reacting with ozone is usually determined by batch experiments with addition of excess *tert*-butyl alcohol (*t*-BuOH) to inhibit potential $\cdot OH$ reactions (Acero et al., 2001; Sánchez-Polo et al., 2008). From the relationship between the CT (concentration $\times$ time) value of ozone and the logarithmic decrease of a target compound, the rate constant can be derived. In this work, the degradation rate of OMT is difficult to measure through batch experiments due to its low reactivity towards ozone. In addition, the presence of excess *t*-BuOH may notably affect the CT value of ozone, since *t*-BuOH reacts towards ozone at a rate constant comparable to that of OMT ($k_{O_3, t-BuOH} = 0.003 \text{ M}^{-1} \text{ s}^{-1}$, Hoigné and Bader, 1983). On the other side, the reaction between OMT and $\cdot OH$ proceeds so fast that its rate constant cannot be measured by batch experiments either. Therefore, competition kinetics was adopted to determine the reaction rate constants of OMT with molecular ozone (direct reaction) and $\cdot OH$ (indirect reaction) in this study.

Semi-continuous experiments were conducted to simulate the pseudo-first-order reactions. *p*CBA was selected as a reference compound because it reacts slowly with molecular ozone but very quickly with $\cdot OH$ ($k_{O_3, pCBA} = 0.15 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\cdot OH, pCBA} = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Sánchez-Polo et al., 2008). Ozone, produced from dried oxygen gas with an ozone generator (3S-A3G, Tonglin, Beijing), was continuously bubbled into a cylindrical glass reactor containing 500 mL ultrapure water (10 mM phosphate buffer, pH 7.5). The aqueous ozone concentration was maintained approximately at a

desired steady-state level by adjusting the electric current of the ozone generator. The stock solutions of OMT and pCBA were added simultaneously into the reactor to initiate reaction. For the reaction of OMT with ozone, *t*-BuOH was added as a scavenger for $\cdot\text{OH}$. It was calculated that, using an equation reported previously (West-erhoff et al., 1999), about 90% of $\cdot\text{OH}$ could be scavenged by the excess *t*-BuOH at an applied concentration of 154 mg L^{-1} . While for the reaction of OMT with $\cdot\text{OH}$, H_2O_2 was added to promote the production of $\cdot\text{OH}$. Water samples were withdrawn at pre-selected time intervals, and the residual ozone was immediately quenched with a dilute Na_2SO_3 solution.

2.4. Identification of degradation byproducts

Semi-continuous experiments were also carried out for Fe@AC-catalyzed ozonation of OMT, in which the degradation byproducts were identified. A desired volume of OMT stock solution and 0.10 g catalyst were added into a cylindrical glass reactor containing 500 mL ultrapure water (initial pH 8.0, adjusted with NaOH and HCl solutions). Phosphate buffer was not used here considering that phosphate ion, as a degradation byproduct of OMT, was to be quantitatively determined. Ozone gas was continuously bubbled into the reaction solution. Water samples were taken at pre-selected time intervals, immediately purged with nitrogen gas to remove the residual ozone, and then filtered off catalyst particles with $0.45 \mu\text{m}$ membrane filters.

In the catalytic ozonation with Fe@AC, a small amount of ferric ions may leach from the catalyst and combine with phosphate (released from OMT degradation) to form ferric phosphate precipitates. This could lead to an underestimate of the phosphate concentration. Therefore, for the measurement of inorganic anions, water samples were acidified to pH 2.0 using HCl solution to dissolve the ferric phosphate precipitates before membrane filtration. For GC/MS analysis of high-molecular-weight (HMW) organic byproducts (e.g., TMP and STMP), water samples were acidified to pH 2.0 to prevent potential hydrolysis of organic byproducts under alkaline conditions, and then SPE was applied.

3. Results and discussion

3.1. Rate constants of OMT reacting with ozone and $\cdot\text{OH}$

Fig. 1 shows that the plot of $\ln(C_{\text{OMT}}/C_{\text{OMT},0})$ vs. $\ln(C_{\text{pCBA}}/C_{\text{pCBA},0})$ exhibited a good linearity for both molecular ozone and $\cdot\text{OH}$ reactions. Consequently, the second-order rate constant of OMT reacting with ozone ($k_{\text{O}_3,\text{OMT}}$) was calculated to be $0.04 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7.5 and 20°C by using Eq. (1) (Fig. 1A) as follows:

$$\frac{k_{\text{O}_3,\text{OMT}}}{k_{\text{O}_3,\text{pCBA}}} = \ln \frac{C_{\text{OMT}}}{C_{\text{OMT},0}} / \ln \frac{C_{\text{pCBA}}}{C_{\text{pCBA},0}} \quad (1)$$

Similarly, the second-order rate constant of OMT reacting with $\cdot\text{OH}$ ($k_{\text{OH},\text{OMT}}$) was calculated to be $5.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7.5 and 20°C (Fig. 1B).

It is noted that OMT does not dissociate in water, so solution pH has no influence on the rate constant of OMT reacting with either ozone or $\cdot\text{OH}$. R_{ct} , a concept defined as the ratio of $\cdot\text{OH}$ to ozone exposure, can be used to express the oxidation potential of an ozonation process for a target compound (von Gunten, 2003). Therefore, the fraction of OMT degraded by ozone (f_{O_3}) can be expressed as follows:

$$f_{\text{O}_3} = \frac{k_{\text{O}_3,\text{OMT}}}{k_{\text{OH},\text{OMT}}R_{\text{ct}} + k_{\text{O}_3,\text{OMT}}} \quad (2)$$

In ozonation of various natural waters, the value of R_{ct} typically ranges from 10^{-9} to 10^{-7} (von Gunten, 2003). As a result, with the values of $k_{\text{O}_3,\text{OMT}}$ and $k_{\text{OH},\text{OMT}}$ being determined, f_{O_3} was calculated

Fig. 1. Determination of reaction rate constants of OMT with O_3 (A) and $\cdot\text{OH}$ (B). Experimental conditions: Temp. = 20°C , pH = 7.5; A: $[\text{O}_3] = 4.3 \text{ mg L}^{-1}$, $[\text{t-BuOH}]_0 = 154 \text{ mg L}^{-1}$, $[\text{OMT}]_0 = 0.84 \text{ mg L}^{-1}$, $[\text{pCBA}]_0 = 0.74 \text{ mg L}^{-1}$; B: $[\text{O}_3]_0 = 0.5 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 0.35 \text{ mg L}^{-1}$, $[\text{OMT}]_0 = 4.49 \text{ mg L}^{-1}$, $[\text{pCBA}]_0 = 3.74 \text{ mg L}^{-1}$.

Fig. 2. GC/MS chromatogram of OMT degradation sample in catalytic ozonation (reaction time = 120 min).

to only range from 0.1% to 7.0% in natural waters. It is clearly seen that OMT was predominantly oxidized by $\cdot\text{OH}$, while the direct oxidation by molecular ozone was insignificant. Therefore, advanced oxidation processes producing abundant $\cdot\text{OH}$ are recommended for OMT removal from water.

3.2. Identification of HMW degradation byproducts

The water sample at a reaction time of 120 min in the catalytic ozonation was withdrawn, pretreated with SPE, and analyzed by GC/MS. Fig. 2 shows that six degradation byproducts of HMW were detected with retention times of 10.5, 16.3, 16.8, 17.3, 18.1, 18.8 min, respectively.

Fig. 3 displays the mass spectra and chemical structures of OMT and its HMW degradation byproducts. OMT with retention time

38.8 min had a molecular ion at m/z 213. The ions at m/z 156 and 110 could correspond to $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{SCH}_2-$ and $(\text{CH}_3\text{O})_2\text{P}(\text{O})-$, respectively.

Comparing with the National Institute of Standards and Technology (NIST) library, the probability of compound 1 (**C1**) being TMP was 94%. Moreover, the retention time and mass spectrum of **C1** were identical to those of the TMP authentic standard. A molecular ion at m/z 140 was observed, which could lose two methyl (CH_3-) groups to yield m/z 110 or lose three CH_3- groups

Fig. 3. Mass spectra of OMT and high-molecular-weight degradation byproducts formed in catalytic ozonation.

Fig. 4. Formation of low-molecular-weight organic acids and inorganic anions during OMT degradation by catalytic ozonation. Experimental conditions: Temp. = 20 °C, pH₀ = 8.0, [OMT]₀ = 10.0 mg L⁻¹, [O₃]₀ = 15.0 mg L⁻¹, Fe@AC dose = 200 mg L⁻¹. The error bars represent the standard deviation of duplicate experiments.

Fig. 5. Degradation of OMT and formation of P-containing byproducts as a function of reaction time in catalytic ozonation. Experimental conditions were the same as in Fig. 4. The error bars represent the standard deviation of duplicate experiments. Mass balance was based on phosphorus atom.

to yield m/z 95. In fact, TMP has been reported as a major byproduct generated from oxidation of other OPPs. For example, it was detected in the oxidation of dichlorvos by permanganate (Liu et al., 2009). TMP was also identified to be a byproduct from the degradation of dichlorvos and dimethoate in a TiO₂-mediated photocatalytic process, which could be further oxidized to *O,O*-dimethyl phosphonic ester (Evgenidou et al., 2006).

Compound 2 (**C2**) with retention time 16.3 min could correspond to pyrrolidin-2-one. Its matching probability reached 95% by comparing with the NIST library. **C2** had a molecular ion at m/z 85, and the ion at m/z 56 was $-\text{CH}_2\text{CH}_2\text{C}(\text{O})-$. **C2** has never been reported as an OMT byproduct before.

Compound 3 (**C3**) with retention time 16.8 min could correspond to *N*-methyl-2-sulfanylacacetamide through comparing its mass spectrum with that reported in a previous study (Bai et al., 2009). **C3** had a molecular ion at m/z 105, which lose $\text{HS}-$ to yield m/z 72 or lose HSCH_3- to yield m/z 58.

Compound 4 (**C4**) was likely to be 2-(methylthio)acetamide with a probability of 85% matching the NIST library. It had a molecular ion at m/z 105, which could lose $\text{NH}_2\text{C}(\text{O})-$ to give m/z 61 or lose $\text{CH}_3\text{S}-$ to give m/z 58. **C4** was first identified as an OMT byproduct.

Compound 5 (**C5**) with a molecular ion at m/z 156 and retention time 18.1 min could correspond to STMP, which matched the NIST library with a probability of 91%. Its mass spectrum and retention time were identical to those of the STMP authentic standard. The fragment ions at m/z 141 and 125 could originate from the loss of CH_3- and $\text{CH}_3\text{O}-$ from the molecular ion, respectively. It has been reported that photo- and thermal-degradation of dimethoate would produce STMP (Andreozzi et al., 1999; Bai et al., 2009).

Compound 6 (**C6**) was verified to be *N*-methyl-2-(methylthio)acetamide through comparing its mass spectrum with that reported in literature (Evgenidou et al., 2006). It had a molecular ion at m/z 119, and the ion at m/z 73 might result from the loss of $\text{CH}_3\text{S}-$. The other two characteristic ions at m/z 58 and 61 were identical with those of **C4**.

In addition, our control experiments showed that less than 5% of OMT was hydrolyzed after 24 h in the pH range of 6.5–8.5. Comparing with the 120 min reaction time in catalytic ozonation, the hydrolysis of OMT could be ignored. Thus, the above six major byproducts were generated from the oxidation rather than the hydrolysis of OMT.

3.3. Formation of LMW organic acids and inorganic anions

In the catalytic ozonation, the solution pH decreased gradually from initial 8.0 to final 4.8 after 120 min reaction, which implies that some organic acids should have been produced from the degradation of OMT. Through IC analysis of water samples, three LMW organic acids including formic, acetic and oxalic acids were detected with final concentrations of 4.0, 12.4 and 28.5 μM, respectively (Fig. 4). In the ozonation of alachlor, formic, acetic, propionic, monochloroacetic, and oxalic acids were also detected (Qiang et al., 2010). Once formed, these LMW organic acids are difficult to mineralize by either molecular ozone or $\cdot\text{OH}$ (Li et al., 2012), thus accumulating in the reaction solution along with the degradation of OMT. For drinking water treatment, biological activated carbon filtration following catalytic ozonation seems to be a feasible option for further mineralization of these LMW organic acids so as to achieve a higher efficiency of TOC removal.

A few inorganic anions were also detected in the catalytic ozonation, including nitrate, sulfate, and phosphate (Fig. 4). These anions came from the partial mineralization of some specific moieties of OMT, which were also detected in photocatalytic ozonation of phorate (Ku and Lin, 2002). After 120 min of reaction time, the concentration of phosphate reached 15.5 μM. Note that the toxicity of OPPs is mainly caused by the $\text{P}=\text{O}$ or $\text{P}=\text{S}$ bond, so the release of phosphorus from OMT would considerably reduce the toxicity of the reaction solution. A high concentration of nitrate was observed, which was released from the Fe@AC catalyst (synthesized from activated carbon and ferric nitrate). Though the final concentration of nitrate increased up to 8.8 mg L⁻¹ after 120 min reaction at a Fe@AC dose of 200 mg L⁻¹, it was still below the maximum contamination level (10.0 mg L⁻¹, as regulated by the Drinking Water Quality Standards of China, GB 5749-2006). In consideration of practical application to water treatment, the dose of Fe@AC is usually below 20 mg L⁻¹ (Ling et al., 2011), at which much less nitrate ions will release from the catalyst.

3.4. Quantification of TMP and STMP

The evolution of TMP and STMP along with the degradation of OMT as a function of reaction time is displayed in Fig. 5. At the reaction time of 120 min, the concentrations of TMP and STMP were 4.4 and 0.4 μM, respectively. A mass balance on phosphorus atom was attempted on the basis of the mean concentrations of TMP, STMP and PO_4^{3-} at various reaction times. The mass balance was close to 100% during the whole reaction course, indicating that

Fig. 6. Proposed pathways of OMT degradation by catalytic ozonation.

the major P-containing byproducts of OMT degradation have been accounted for (Fig. 5).

3.5. Proposed pathways of OMT degradation

Under the experimental conditions for the catalytic ozonation of OMT, the value of f_{O_3} was calculated to be always below 17% during the whole reaction course (i.e., 120 min). Thus, $\cdot\text{OH}$ was a primary oxidant accounting for OMT degradation. Based on the identified byproducts, the reaction pathways of OMT degradation were proposed, as illustrated in Fig. 6. The sulfur atom in OMT was the most electronegative, so the sulfated bonds tended to be attacked first by the oxidant (i.e., $\cdot\text{OH}$). The loss of one electron from sulfur led to the cleavage of either P–S or S–C bond. The cleavage of P–S bond would produce $\cdot\text{SCH}_2\text{C}(=\text{O})\text{NHCH}_3$ and $[(\text{CH}_3\text{O})_2\text{P}(\text{O})]^\cdot$, and then lead to the formation of **C1** (TMP), **C3** and **C6** (Evgenidou et al., 2006). A continuous attack by $\cdot\text{OH}$ to **C6** on the N–C bond yielded **C4**. On the other side, the cleavage of S–C bond would produce $[\text{CH}_3\text{NHC}(\text{O})\text{CH}_2]^\cdot$ and $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{S}^\cdot$, and then lead to the formation of **C2** and **C5** (STMP). The oxidation of sulfur atom in **C5** led to the formation of **C1** (TMP). As shown in Fig. 5, STMP had a much lower concentration than TMP throughout the reaction course, implying that STMP was much easier to be oxidized. Further oxidation of **C1**, **C2**, **C3** and **C4** as well as direct attack of the side chains of OMT would produce LMW organic acids (i.e., formic, acetic and oxalic acids) and inorganic anions (i.e., nitrate, sulfate and phosphate).

3.6. Toxicity change of OMT solution

Risk index (RI), as defined in Eq. (3) (Sinclair et al., 2006), was applied to assess approximately the toxicity variation of the reaction solution during the catalytic ozonation:

Fig. 7. Variation of risk index (RI) during OMT degradation by catalytic ozonation. Experimental conditions were the same as in Fig. 4.

$$RI = \sum \frac{f_i}{LD_{50,i}} \quad (3)$$

where f_i represents the molar percentage of compound i with respect to the initial OMT concentration; $LD_{50,i}$ represents the oral LD_{50} in rats of compound i . The larger the RI, the greater the toxicity of the reaction solution.

It is well known that the P=O bond of OPPs can inhibit acetylcholinesterase, which leads to accumulation of acetylcholine in mammal bodies (Pope et al., 2005). Therefore, if a byproduct generated from OMT degradation retains the P=O bond, it still has an acute toxicity. For example, the oral LD_{50} values in rats are 840 and

15 mg kg⁻¹ for TMP and STMP, respectively (Mallipudi et al., 1979; Meister, 1991). The toxicity of STMP is two times as high as that of OMT (i.e., 30 mg kg⁻¹) (NCILB, 1973). As shown in Fig. 7, the overall RI value of the reaction solution gradually decreased as the catalytic ozonation proceeded, indicating partial detoxification of the OMT solution. This may be explained by the release of PO₄³⁻ from OMT. The residual toxicity was mainly caused by the undegraded OMT. Though STMP is more toxic than OMT, its low concentration resulted in an insignificant effect on the overall toxicity of the reaction solution.

4. Conclusions

The reaction rate constants of OMT with ozone and ·OH were 0.04 and 5.3 × 10⁸ M⁻¹ s⁻¹ at pH 7.5 and 20 °C, respectively. OMT was mainly oxidized by ·OH, while its direct oxidation by molecular ozone was insignificant. OMT degradation was initiated by ·OH attack to its sulfated bonds in catalytic ozonation. TMP and PO₄³⁻ were two major P-containing byproducts from OMT degradation. The release of PO₄³⁻ from OMT led to a significant decrease in the solution toxicity, indicating that the catalytic ozonation with Fe@AC is a safe technology for OMT removal from water. The residual TOC consisted of LMW organic acids, so biological activated carbon filtration following catalytic ozonation tended to achieve a higher TOC removal in drinking water treatment.

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