



Deiodination of iopamidol by zero valent iron (ZVI) enhances formation of iodinated disinfection by-products during chloramination

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ABSTRACT

Iodinated X-ray contrast media (ICM) is considered as one of iodine sources for formation of toxic iodinated disinfection byproducts (I-DBPs) during disinfection. This study investigated transformation of a typical ICM, iopamidol (IPM) by zero valent iron (ZVI) and the effect of transformation on the formation of I-DBPs during chloramination. It was found that the presence of ZVI could deiodinate IPM into I^- and the transformation of IPM exhibited a pseudo-first-order kinetics. Acidic circumstance, SO_4^{2-} , Cl^- and monochloramine could promote the transformation of IPM by ZVI, while SiO_3^{2-} inhibited the transformation of IPM. Moreover, the transformation of IPM by ZVI changed both the formed species and amounts of I-DBPs during chloramination. During the chloramination of IPM-containing water, $CHCl_2I$ and iodoacetic acid were the predominant iodinated trihalomethanes (I-THMs) and iodinated haloacetic acids (I-HAAs), respectively in the absence of ZVI, while CHI_3 and triiodoacetic acid became the predominant ones with 1.0 g L^{-1} ZVI. The addition of 5.0 g L^{-1} ZVI increased I-DBPs formation amounts by 6.0 folds after 72 h and maximum formation of I-DBPs occurred at pH 5.0. Enhanced I-DBPs formation was also observed with various real water sources. Given that ZVI ubiquitously exists in the unlined cast iron distribution pipes, the deiodination of IPM by ZVI during distribution may increase the formation of I-DBPs, which needs receive enough attention.

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1. Introduction

Because of their potential adverse health effects, disinfection by-products (DBPs) formation during water treatment and distribution is one of the great concerns (Hu et al., 2016; Dong et al., 2017). Many water utilities have switched disinfectant from free chlorine to monochloramine (NH_2Cl) to comply with the increasingly stringent regulatory limits for trihalomethanes (THMs) and haloacetic acids (HAAs) (Liu et al., 2017). However, the formation of emerging DBPs (e.g. iodinated DBPs (I-DBPs) and nitrosodimethylamine) and potential release of lead ions during chloramination may increase new public perception of drinking water quality (Arnold and Edwards, 2012; Sakai et al., 2016; Liu et al., 2017).

Formation of toxic I-DBPs is a growing concern for water utilities. It has been verified that I-DBPs generally are more cytotoxic, genotoxic and developmental toxic than their chlorinated or brominated analogs (Richardson et al., 2008; Yang and Zhang, 2013). The iodine source for the I-DBPs formation including inorganic iodide (I^-) and iodine-containing organic compound (Wang et al., 2014). As a medical diagnostic agent used for imaging blood vessels and organs in iodinated X-ray contrast media, iopamidol (IPM) is among the most recalcitrant and highly persistent pharmaceuticals in the aquatic environment (Seitz et al., 2006; Oulton et al., 2010). Increasing concentrations of IPM have been detected in the hospital and domestic wastewater, treated wastewater effluent, surface water, groundwater, and even finished drinking water, with concentration up to $\mu\text{g L}^{-1}$ level (Echeverria et al., 2013). As the iodine element of IPM is up to 50%, IPM not only contributes substantially to the total organic iodine in water but also acts as a potential iodine source for the formation I-DBPs

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(Duirk et al., 2011).

Continued efforts have been made to identify the formation mechanism and pathway of I-DBPs with different iodine sources (i.e., organic iodine-containing compound and inorganic I^-) during disinfection (Duirk et al., 2011; Yan et al., 2016; Xia et al., 2017). Wang et al. (2014) reported that the chloramination of I^- exhibited much higher I-DBPs formation than that of IPM. Duirk et al. (2011) found that both the formation amounts and species of I-DBPs during chloramination differed with inorganic and organic iodine sources. Dichloroiodomethane ($CHCl_2I$) dominated the formed I-DBPs when IPM was the iodine source, whereas the most abundant I-DBPs was iodoform (CHI_3) during the chloramination of I^- and NOM. The transformation of IPM during water treatment and distribution processes may induce the release of inorganic I^- from IPM, which would influence the formation amount and species of I-DBPs (Wendel et al., 2016).

Unlined cast iron pipe is widely adopted in the distribution of drinking water from DWTPs to consumers for several centuries all over the world (Zhu et al., 2014). As a kind of highly reactive, cost-effective and environment-friendly material, zero-valent iron (ZVI) has been extensively employed to remove various contaminants via releasing electrons to target compound (Noubactep, 2015). It has been verified that the presence of ZVI in the unlined cast iron distribution pipe could promote or diminish the formation of DBPs during drinking water distribution (Wang and Zhu, 2010; Xia et al., 2017). Chu et al. (2016a) observed that dichloroacetamide can be formed in the absence of chlorinated disinfectants through reduction of three chloramphenicol antibiotics by ZVI, which provided new insights to rethink the effect of distribution process on the formation pathway of DBPs. Meanwhile, various halogenated organic molecules are susceptible to ZVI reduction, including haloacetic acids, halonitromethane, trichloroethylene, and polychlorinated biphenyls (Chu et al., 2016b; Pearson et al., 2005; Yin et al., 2016). Recently, Xia et al. (2017) found that highly cytotoxic iodinated trihalomethanes could be generated from iodate-containing waters in the presence of ZVI during chloramination. The reduction of IO_3^- to I^- by ZVI and subsequent oxidation of I^- by chloramine enhance the formation of I-DBPs. As most water distribution networks contain unlined cast iron pipes, the presence of ZVI in cast iron pipes may induce the deiodination of IPM and the release of I^- . However, the transformation of IPM during drinking water distribution and the effects of IPM transformation on the formation I-DBPs during chloramination were rarely reported.

The objectives of this study were to: (1) investigate the transformation of IPM by ZVI; (2) clarify the effects of water matrix on the transformation of IPM by ZVI; (3) investigate the effect of IPM transformation by ZVI on toxic I-DBPs formation during chloramination. It is expected to illustrate the behavior and fate of IPM during distribution to understand the potential I-DBPs formation mechanisms and pathways.

2. Materials and methods

2.1. Materials

All chemicals used in this study were reagent grade or higher. Individual I-DBPs including chlorodiiodomethane ($CHCl_2I$), dichloroiodomethane ($CHCl_2I$), iodoacetic acid (IAA) and diiodoacetic acid (DIAA) were all purchased from CanSyn Chem. Co. (New Westminister, BC, Canada). CHI_3 (99%), triiodoacetic acid (TIAA, 90%) and iopamidol (99%) were obtained from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile and methanol were purchased from Thermo Fisher Scientific (Waltham, MA, USA) at high-performance liquid chromatography (HPLC) grade purity and formic acid ($\geq 99.0\%$) was from Dikma Technologies (Lake Forest, CA, USA).

Suwannee River NOM isolate (2R101N) was obtained from the International Humic Substances Society. ZVI (100 mesh, $\geq 98.0\%$), $(NH_4)_2SO_4$ (99%) and NaOCl (5% of active chlorine) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). All other chemicals, of at least analytical grade, were provided by Beijing Chemical Reagents Company (Beijing, China). All solutions were prepared in ultrapure water ($18.2 M\Omega\text{ cm}$) produced by a Milli-Q system (Advantage A10, Millipore, MA, USA).

2.2. Experimental procedures

2.2.1. Transformation of IPM by ZVI

The experiments were performed in a series of 100 mL glass vials at ambient temperature ($25\text{ }^\circ\text{C}$). To initiate the reaction, ZVI was dosed into the glass vials, each of which contained 50 mL solution spiked with $10\text{ }\mu\text{M}$ IPM. These vials were sealed immediately and placed on a shaker (100 rpm). Factors including ZVI dosage ($0\text{--}10.0\text{ mg L}^{-1}$) and NH_2Cl dosage ($0\text{--}0.4\text{ mM}$) on the formation of I-DBPs were investigated. Typically, the initial experimental conditions were as follows: $10\text{ }\mu\text{M}$ IPM, 5.0 g L^{-1} ZVI, and pH 7.0, unless otherwise specified. At regular time intervals, an aliquot of 1.0 mL suspension was withdrawn and filtered with $0.22\text{ }\mu\text{m}$ syringe filter before the chemical analysis.

2.2.2. Effect of deiodination of IPM on I-DBPs formation

All experiments were performed in triplicate using 50-mL amber glass bottles with polytetrafluoroethylene-lined septum screw-caps under headspace-free conditions at ambient temperature ($25\text{ }^\circ\text{C}$). NH_2Cl solution was freshly prepared by adding a desired amount of NaOCl stock solution to an $(NH_4)_2SO_4$ solution (10 mM bicarbonate buffer, pH 8.5) at a Cl/N molar ratio of 0.7:1 (Vikesland et al., 2001). To initiate the reaction, NH_2Cl was dosed into the glass vials. Factors including ZVI dosage ($0\text{--}10.0\text{ g L}^{-1}$), DOC ($0\text{--}10.0\text{ g L}^{-1}$) and NH_2Cl dosage ($0\text{--}0.2\text{ mM}$) on the formation of I-DBPs were investigated. Typically, the initial experimental conditions were as follows: 5 g L^{-1} ZVI, 0.04 mM NH_2Cl , $10\text{ }\mu\text{M}$ IPM and 2.0 mg L^{-1} DOC, unless otherwise specified. After 72 h, an aliquot of 20 mL suspension was withdrawn and filtered through $0.45\text{ }\mu\text{m}$ membrane before the chemical analysis.

2.2.3. I-DBPs formation with real waters

To investigate the effect of water matrix on I-DBPs formation during chloramination of IPM-containing water with ZVI, $500\text{ }\mu\text{g L}^{-1}$ IPM was spiked into four real waters including the raw and filtered waters of a ground water (GW)-based and a surface water (SW)-based drinking water treatment plant in Beijing, whose major quality parameters are summarized in Table S1. These water samples were filtered through $0.45\text{ }\mu\text{m}$ membrane and stored at $4\text{ }^\circ\text{C}$ until use.

2.3. Analysis

IPM was detected with an Agilent 1200 Series HPLC system equipped with an Atlantis C18 column ($4.6 \times 250\text{ mm}$, $5.0\text{ }\mu\text{m}$) at UV wavelengths of 242 nm . The mobile phase was a mixture of methanol/water ($85/15$, v/v) at a flow rate of 1.0 mL min^{-1} . The injection volume was $50\text{ }\mu\text{L}$, and the column temperature was maintained at $25\text{ }^\circ\text{C}$. The limit of quantitation of IPM by HPLC was determined to be $8.0\text{ }\mu\text{g L}^{-1}$. I^- concentration was analyzed by ion chromatography (ICS-2000, Dionex, CA, USA) with an AS19 column ($4 \times 250\text{ mm}$) and an eluent of 30 mM KOH at a flow rate of 1 mL min^{-1} . Water samples were filtered ($0.45\text{ }\mu\text{m}$) prior to chromatographic analysis and the injection volume was $20\text{ }\mu\text{L}$. Dissolved organic carbon (DOC) concentration was measured with a TOC-VCPN analyzer (Shimadzu, Japan).

CHCl_2I , CHClI_2 and CHI_3 were analyzed after samples being extracted with methyl *tert*-butyl ether using a gas chromatograph (7890, Agilent, CA, USA) equipped with an HP 5 capillary column (30 m \times 0.25 mm, 0.25 μm , J&W, USA) and an electronic capture detector based on the modified USEPA method 551.1 (USEPA Method 551.1, 1995). IAA, DIAA and TIAA were analyzed by liquid/liquid extraction with methyl-*tert*-butyl-ether (MtBE), derivatization with acidified methanol, and quantification by GC/ECD with the same capillary column based on the modified USEPA method 552.2 (USEPA Method 552.2, 1995). The LOQs were in the range of 0.1–1.0 $\mu\text{g L}^{-1}$ for iodinated trihalomethanes (I-THMs) and iodinated haloacetic acids (I-HAAs) as described in our previous study (Liu et al., 2017). Concentrations of NH_2Cl were determined using the standard DPD method (Rice et al., 2012).

3. Results and discussion

3.1. Transformation of IPM by ZVI

The effect of ZVI dosage on the degradation of IPM is shown in Fig. 1. The degradation of IPM by ZVI is a slow process. IPM was not completely degraded after 72 h with ZVI dosage up to 10 g L^{-1} . Stieber et al. (2011) compared the degradation rates of various micro-pollutants with ZVI and the degradation rates of two iodinated X-ray contrast media were obviously lower than those of ciprofloxacin, cefuroxime and methotrexate. When the initial dosage of ZVI increased from 0.5 to 5.0 g L^{-1} , the removal efficiency of IPM after 72 h increased from 12.8% to 60.8%. However, with the further increase of ZVI dosages to 7.5 and 10 g L^{-1} , the removal efficiencies of IPM after 72 h exhibited decreasing trends compared with 5.0 g L^{-1} ZVI. Li et al. (2008) also found that higher ZVI dosage resulted in the higher Cr(VI) reduction rate. However, over dosed ZVI may induce the particle aggregation of ZVI, which decreases the reactivity of ZVI. During the transformation of IPM, the total organic carbon of the solution remained unchanged (data not shown), indicating that the transformation of IPM by ZVI played a major role while the adsorption of IPM to ZVI is neglectable.

The evolution of IPM with ZVI was further evaluated with a kinetic model. It was found that the concentration of IPM exhibited a pseudo-first-order kinetics within 6 h, showing a linear dependence of $\ln(C/C_0)$ on time with a good correlation ($R^2 > 0.98$). If plotting the k_{obs} values as a function of initial ZVI concentration (0.5–5.0 g L^{-1}), a linear correlation (0.02–0.18 h^{-1}) with a zero

intercept was observed (Fig. S1), indicating that the reaction was also of first-order with respect to ZVI.

$$d[\text{IPM}]/dt = k_{\text{obs}}[\text{IPM}] \quad (1)$$

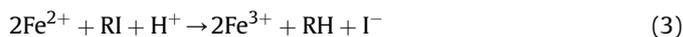
where [IPM] is the concentration of IPM (μM), t is time (h) and k_{obs} is observed reaction rate constants (h^{-1}).

Previous studies showed that the reduction of halogenated organic compound could be described by two different mechanisms including direct and indirect reductions (Li and Farrell, 2000; Stieber et al., 2011). The direct reduction may occur after formation of a chemisorption complex (Eqs. (2)–(3)) or by electron tunneling to the physically adsorbed compound which is separated from the iron surface by adsorbed water or an oxide film. The indirect reduction is suggested as a reaction of the organic compounds with adsorbed atomic hydrogen (H_{ads}) by the formation of chemisorbed hydride complexes as described in Eqs. (4)–(5).

(I) Direct electron transfer from ZVI at the metal surface:



(II) Reduction by Fe^{2+} , which results from the corrosion of ZVI:



(III) Catalytic hydrogenation by atomic hydrogen formed by reduction of H_2O or acidic iron corrosion:



As shown in Eqs. (2)–(5), both the direct and indirect reductions of IPM by ZVI would induce the release of I^- . The evolution of I^- concentration during the transformation of IPM by ZVI was shown in Fig. S2. There existed a lag period for release of I^- within 2 h. At the beginning, the released I^- from IPM may be very reactive and could re-incorporate to organic matter easily (Yan et al., 2016), which induced this lag period. After the lag period, the concentration of I^- increased with the transformation of IPM. The released concentration of I^- reached 2.9 μM after 72 h (9.6% of the iodine containing in IPM). The transformation of iodine from organic IPM to inorganic I^- by ZVI would influence the I-DBPs formation during chloramination, which needs a further evaluation.

3.2. Effect of water matrix on transformation of IPM by ZVI

It has been widely accepted that the water quality plays a vital role in the surface corrosion of ZVI, which further influences the degradation rate of pollutant. Stachowicz et al. (2008) observed that the existence of anion significantly impacted the removal of contaminants by ZVI. Fig. 2 depicts the influence of water quality including pH, SO_4^{2-} , Cl^- , SiO_3^{2-} and NOM on the removal of IPM by ZVI. As shown in Fig. 2A, the removal of IPM by ZVI was highly pH-dependent. After 72 h, approximately 88.8% of IPM was removed by ZVI at pH 5.0, whereas only 28.8–68.8% of IPM was removed at pH 7.0–9.0 within the same time period. This pH-dependent trend of pollutant removal by ZVI had also been reported previously (Kanel et al., 2006; Sasaki et al., 2009). During the direct reduction, the pH may affect the formation of an oxide film on the ZVI surface and therefore the number of reactive adsorption sites and the distance to the iron surface (Stieber et al., 2011). Meanwhile, a thin layer consisting of a mixture of FeO and $\text{Fe}(\text{OH})_2$ with polymeric

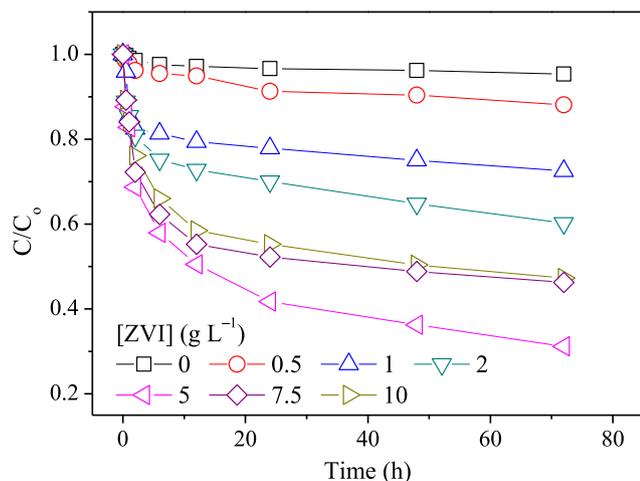


Fig. 1. Effect of initial concentration of ZVI on transformation of IPM. Experimental conditions: $[\text{IPM}]_0 = 10 \mu\text{M}$, pH 7.0, 25 °C.

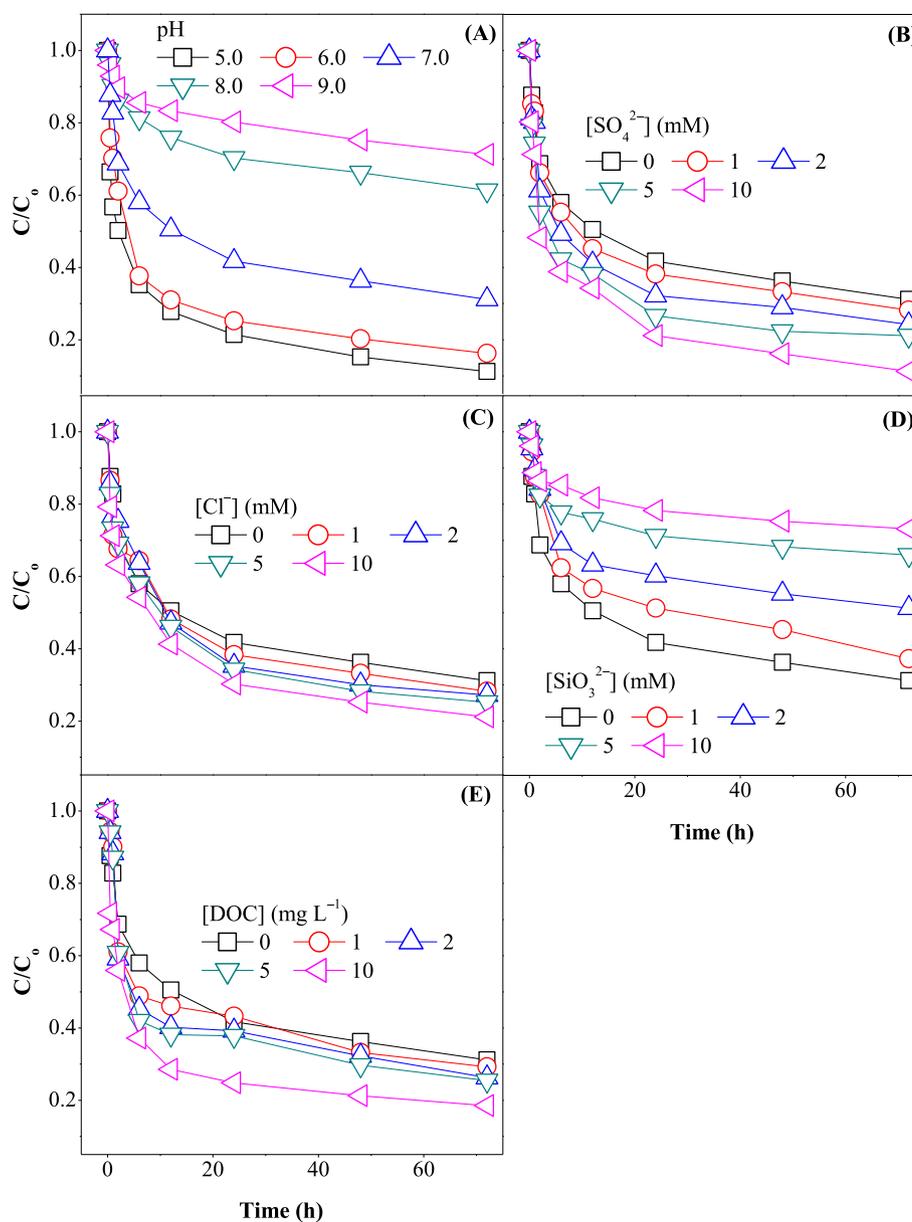


Fig. 2. Effect of water matrix on transformation of IPM with presence of ZVI: (A) pH, (B) SO_4^{2-} , (C) Cl^- , (D) SiO_3^{2-} , (E) HA. Experimental conditions: $[\text{IPM}]_0 = 10 \mu\text{M}$, $[\text{ZVI}]_0 = 5.0 \text{ g L}^{-1}$, 25°C ; pH 7.0 for (B)–(E).

structure would be formed under the acidic circumstance, which does not increase with time and changes slightly to an akaganeite-like structure. However, under neutral or alkaline circumstances the oxidation would lead to the formation of lepidocrocite structure with a continuously increasing surface layer and subsequent a decreasing reaction yield with IPM (Mielczarski et al., 2005).

The effects of different levels of SO_4^{2-} , Cl^- and SiO_3^{2-} on the removal of IPM by ZVI at pH 7.0 were shown in Fig. 2B, C and D, respectively. The presence of SO_4^{2-} or Cl^- promoted the corrosion of ZVI and the removal of IPM. The enhancement of ZVI corrosion in the presence of Cl^- could be explained by the fact that Cl^- is well known to destroy the passive film on ZVI by inducing pitting corrosion (Strehblow and Marcus, 2012). Similarly, SO_4^{2-} could be incorporated into the crystal structure and its inner double layer of iron oxide/hydroxides to promote ZVI corrosion (Tresintsi et al., 2014). After 72 h, the removal of IPM with 10 mM SO_4^{2-} or Cl^- could reach 78.9% and 88.7%, respectively. Promoted ZVI corrosion

with the presence of SO_4^{2-} or Cl^- could provide fresh ZVI, which accelerated the transformation of IPM indirectly.

On the contrary with SO_4^{2-} and Cl^- , SiO_3^{2-} acted as a corrosion inhibitor in Fig. 2D, which could be ascribed to its polymerization and coating effects (Yang et al., 2017). Smith and Edwards (2005) reported that SiO_3^{2-} could be adsorbed on the corrosion products as a barrier as soon as the corrosion of ZVI starts, which then gradually form silica polymers or amorphous solid phases on the ZVI surface to inhibit corrosion. The silica polymer coating on the ZVI surface remarkably inhibited corrosion of ZVI and thus limited fresh ZVI was available for the removal of IPM. Moreover, the shielding effect of the SiO_3^{2-} shell may further block mass transfer as well as the electron transfer pathway between ZVI and IPM. Thus, with the increase of SiO_3^{2-} concentration from 0 to 10 mM, the removal of IPM decreased from 68.8% to 26.8%.

Because of the ubiquitous presence of natural organic matter in the source water and drinking water, different humic acid (HA)

levels (0–10 mgDOC L⁻¹) were adopted to evaluate the impact of NOM on the transformation of IPM by ZVI. It was found that the effect of HA on the removal of IPM by ZVI was not obvious like anions (Fig. 2E). With the increase of HA concentration from 0 to 5.0 mgDOC L⁻¹, the removal efficiencies of IPM by ZVI after 72 h changed slightly (68.8–74.6%). When the NOM concentration increased to 10 mgDOC L⁻¹, the removal of IPM increased to 81.5%. Previous study showed that HA was able to act as the electron shuttle to rapidly transfer electrons, leading to enhanced reductive degradation of contaminants (Doong and Lai, 2005). Meanwhile, the presence of HA could impact the corrosion process of ZVI. Liu and Lo (2011) reported that HA could enhanced the release of dissolved iron in the forms of soluble Fe–HA complexes and stabilized Fe hydroxide colloids, which may suppress the precipitation of iron corrosion products on ZVI surfaces and enhance the removal of pollutant subsequently. The accelerated transformation of IPM by ZVI with the presences of HA indicates that the released I⁻, HA and residual disinfectant (e.g., NH₂Cl or free chlorine) may coexist during the distribution of drinking water, which induces the concern of I-DBPs formation.

3.3. Enhanced formation of I-DBPs induced by deiodination of IPM

Because of the transformation of IPM from organic iodinated compound to inorganic I⁻, the formation species and amounts of I-DBPs from IPM may change correspondingly, which needs a further evaluation. The effect of NH₂Cl on the transformation of IPM by ZVI was firstly investigated. It was found that the transformation of IPM by ZVI could be promoted after the addition of NH₂Cl (Fig. S3). Previous study showed that oxidants including NaClO, KMnO₄ and H₂O₂ could accelerate ZVI corrosion and thereby the removal of heavy metals by ZVI (Guo et al., 2016). Thus, NH₂Cl could promote the IPM transformation via accelerating ZVI corrosion. Meanwhile, the oxidation of released I⁻ by NH₂Cl may promote the deiodination of IPM either.

Fig. 3 exhibits the formation of I-DBPs including CHCl₂I, CHCl₂, CHI₃, IAA, DIAA and TIAA with different ZVI dosages. It was found that the presence of ZVI during the chloramination of IPM-containing water changed both the species and amounts of I-DBPs formed. After 72 h, CHCl₂I and IAA were the predominant species of I-THMs and I-HAAs, respectively in the absence of ZVI. The average formation amount of CHCl₂I was 5.9 ± 0.52 µg L⁻¹, significantly higher than those of other evaluated I-DBPs. The formation amounts of I-HAAs were always lower than those of I-THMs in the presence and absence of ZVI. Duirk et al. (2011) also observed that CHCl₂I and CHCl₂ were the predominant I-THMs formed, and IAA was the predominant I-HAAs formed when chloramination of IPM-containing water and the formation amounts of I-DBPs were comparable to this study. As shown in Fig. 3, both the formation species and amounts of I-DBPs changed obviously with the increase of ZVI dosages. When the initial ZVI dosages increased to 5.0 g L⁻¹, CHI₃ (20.8 ± 1.2 µg L⁻¹) and TIAA (6.9 ± 0.3 µg L⁻¹) became the predominant species of I-THMs and I-HAAs, respectively. The presence of 5.0 g L⁻¹ ZVI increased the formation amounts of I-DBPs 6.0 folds, indicating that the deiodination of IPM by ZVI shifted the iodine source of I-DBPs from organic IPM to inorganic source (I⁻). Compared with the chloramination of IPM, chloramination of I⁻ would quickly form HOI/I₂ (Eq. (6)). Previous studies have shown that the second-order rate constants for the reaction of NOM with HOI and I₂ were in the ranges of 0.1–0.4 M⁻¹ s⁻¹ and (0.4–1.5) × 10⁻⁴ M⁻¹ s⁻¹, respectively (Bichsel and von Gunten, 2000; Warner et al., 2000). The formed HOI/I₂ would react with NOM or the transformation products of IPM to form I-DBPs (Eq. (7)).

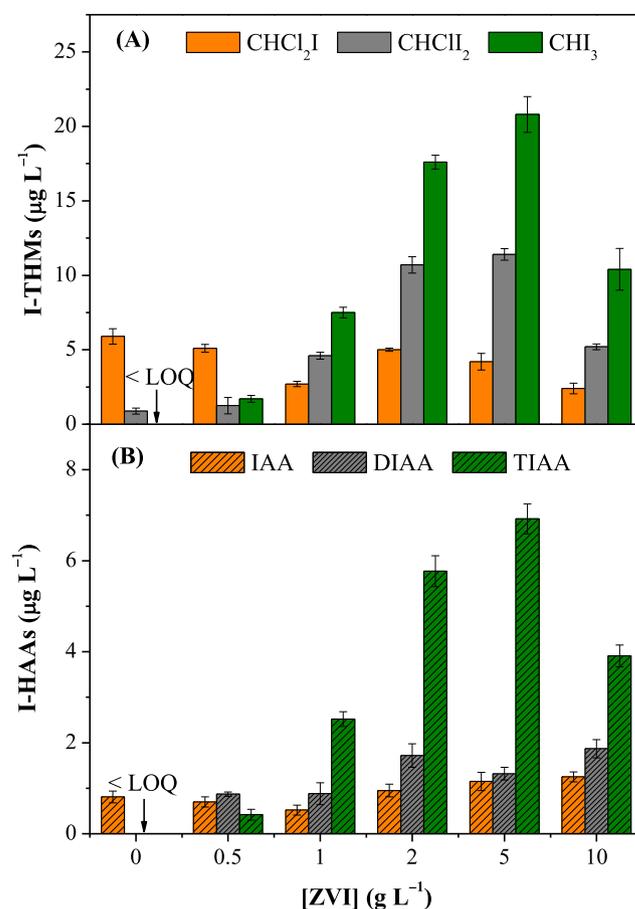
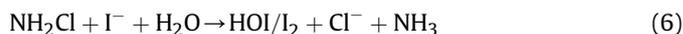


Fig. 3. Effect of initial ZVI dosage on formation of I-THMs (A) and I-HAAs (B) during chloramination of IPM. Experimental conditions: [NH₂Cl]₀ = 0.04 mM, [IPM]₀ = 10 µM, [DOC]₀ = 2.0 mg L⁻¹, pH 7.0, 25 °C, reaction time = 72 h. Error bars represent the 95% confidence interval.



3.4. Effect of NOM and NH₂Cl concentrations on formation of I-DBPs

The effects of NOM and NH₂Cl concentrations on I-DBPs formation were also investigated. Fig. 4 shows the formation of I-DBPs as a function of increasing NOM concentration (expressed as DOC) at pH 7.0. The concentrations of CHI₃ and TIAA increased significantly with increasing DOC concentration from 0 to 2.0 mg L⁻¹, and then decreased at a higher DOC concentration (5.0–10.0 mg L⁻¹), whereas the concentrations of CHCl₂I and IAA remained nearly constant in the presence of NOM. The formation amount of I-DBPs in the absence of NOM was just 8.2 µg L⁻¹, 20.3% of the formation amount of I-DBPs with 1.0 mg L⁻¹ NOM. Obviously, the presence of NOM provided the organic precursor of I-DBPs. The decrease of CHI₃ and TIAA concentrations at 5.0–10.0 mg L⁻¹ DOC was attributable to the fact that triiodo-DBPs were less likely to be formed when excess reaction sites of NOM were available (Liu et al., 2017).

The effect of NH₂Cl dosage (0–0.2 mM) on I-DBPs formation with the presences of IPM, ZVI and NOM is shown in Fig. 5. I-DBPs formation was not observed without NH₂Cl addition, indicating

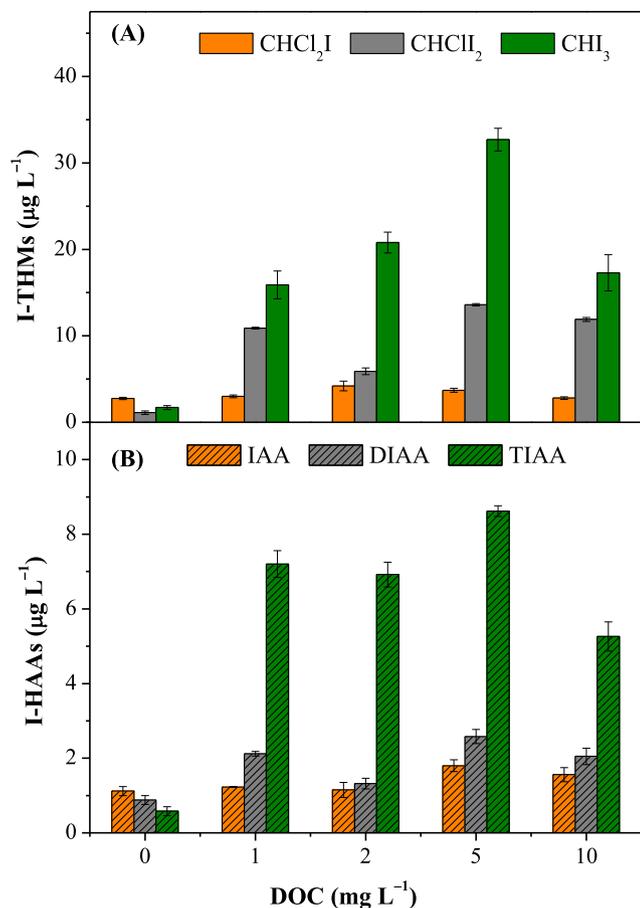


Fig. 4. Effect of initial DOC concentration on formation of I-THMs (A) and I-HAAs (B) during chloramination of IPM with presence of ZVI. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.04 \text{ mM}$, $[\text{IPM}]_0 = 10 \text{ }\mu\text{M}$, $[\text{ZVI}]_0 = 5.0 \text{ g L}^{-1}$, pH 7.0, 25 °C, reaction time = 72 h. Error bars represent the 95% confidence interval.

that HOI/I₂ was not formed during the reduction of IPM by ZVI. After the addition of NH₂Cl, CHI₃ and TIAA were always the predominant I-THMs and I-HAAs species, respectively under the tested NH₂Cl dosages, indicating that the deiodination reaction of IPM by ZVI occurred and inorganic iodine source was abundant for the I-DBPs formation. Xia et al. (2017) also observed that the presence of NH₂Cl could accelerate the reduction of IO₃⁻ to I⁻ via converting I⁻ to HOI/I₂ by chloramine. Meanwhile, all the evaluated I-DBPs concentrations significantly increased with increasing NH₂Cl dosages in the range of 0.01–0.1 mM, and then decreased at 0.2 mM NH₂Cl dosage. The decrease in the I-DBPs concentrations at 0.2 mM NH₂Cl dosage indicated that more I⁻ reduced from IPM may be directly oxidized to IO₃⁻ by free chlorine produced from NH₂Cl hydrolysis, which resulted in less organic I-DBPs formation.

3.5. Effect of pH on formation of I-DBPs

As depicted in Fig. 2A, pH is a vital factor governing the reactivity of ZVI and the deiodination of IPM. Our previous results showed that pH also played important roles in the hydrolysis of NH₂Cl, the reactivity of HOI/I₂ and the formation of I-DBPs during the chloramination of I⁻-containing water (Liu et al., 2017). Thus, the effects of pH on the I-DBPs formation during the chloramination of IPM-containing water with ZVI were investigated (Fig. 6). It was found that acidic circumstances (pH 5.0–6.0) facilitated the I-THMs and I-HAAs formation during the chloramination of IPM-

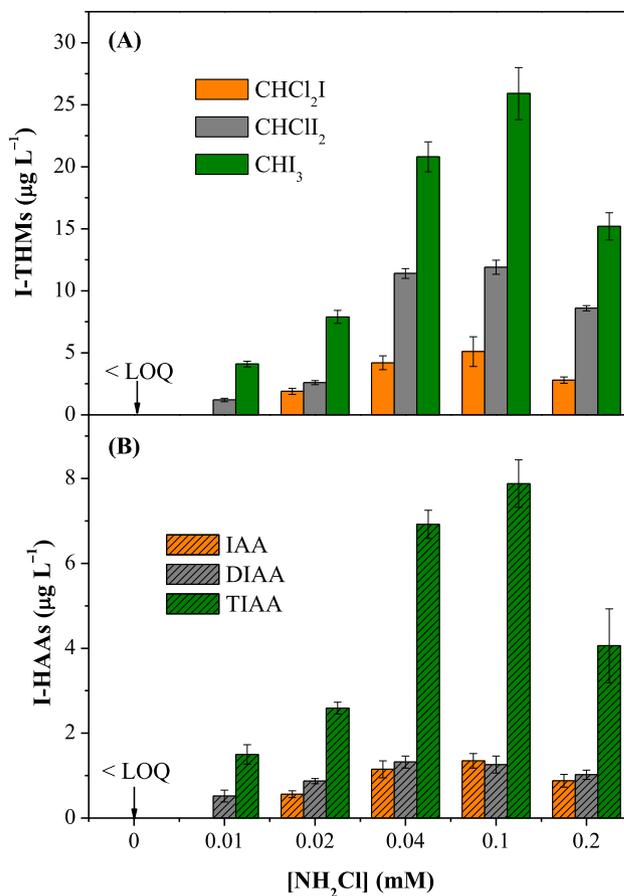


Fig. 5. Effect of initial NH₂Cl dosage on formation of I-THMs (A) and I-HAAs (B) during chloramination of IPM with presence of ZVI. Experimental conditions: $[\text{IPM}]_0 = 10 \text{ }\mu\text{M}$, $[\text{DOC}]_0 = 2.0 \text{ mg L}^{-1}$, $[\text{ZVI}]_0 = 5.0 \text{ g L}^{-1}$, pH 7.0, 25 °C, reaction time = 72 h. Error bars represent the 95% confidence interval.

containing water with ZVI. The CHI₃ and TIAA concentrations decreased obviously from 37.9 ± 1.3 and $12.3 \pm 0.2 \text{ }\mu\text{g L}^{-1}$ at pH 5.0 to 1.8 ± 0.2 and $1.2 \pm 0.2 \text{ }\mu\text{g L}^{-1}$ at pH 9.0, respectively. In general, acidic circumstance favored the formation of I-HAAs, which is similar to the formation of the regulated HAAs at various pH values. However, the most abundant formation of I-THMs formation at pH 5.0 in this study was on the contrary with previous results that neutral and alkaline circumstances are more favorable for I-THMs formation during chloramination of I⁻-containing water (Hua and Reckhow, 2008; Liu et al., 2017). This inconsistency could be ascribed to that the deiodination of IPM by ZVI was preferred under the acidic circumstance, which is also the prerequisite for subsequent I-DBPs formation.

3.6. Enhanced formation of I-DBPs with real waters and environmental implications

To investigate the I-DBPs formation with real water sources, four water samples including the raw and filtered waters of a ground water-based and a surface water-based drinking water treatment plant were spiked with $500 \text{ }\mu\text{g L}^{-1}$ IPM, respectively. Then the I-DBPs formation species and amounts in the presence of 5.0 g L^{-1} ZVI and 0.04 mM NH₂Cl were analyzed after 72 h. Due to the different DOC contents of the four samples, normalized concentrations of I-THMs and I-HAAs by the DOC concentration are shown in Fig. 7. Similar with the HA-spiked water in section 3.3, CHI₃ and TIAA were always the predominant species of I-THMs and I-HAAs

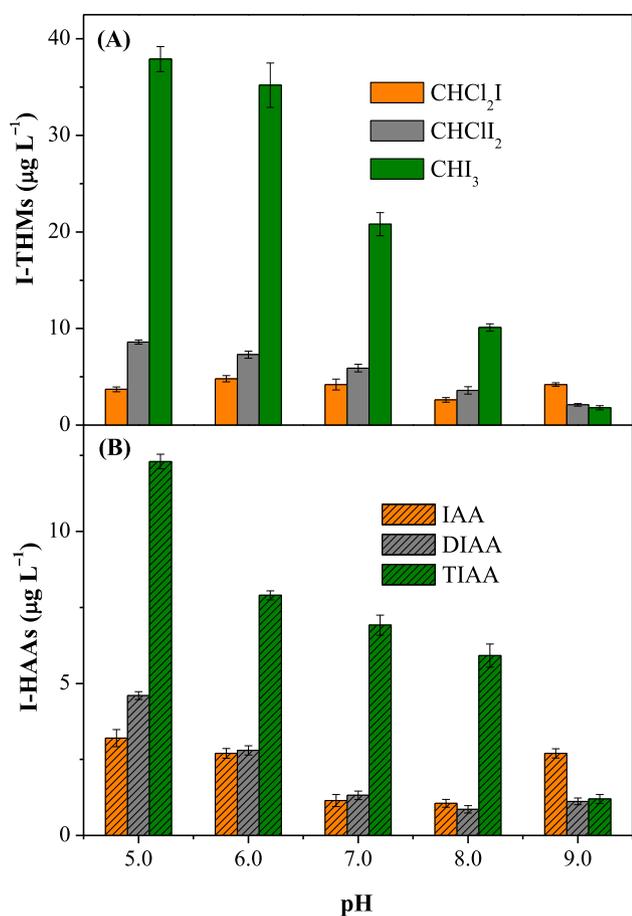


Fig. 6. Effect of pH on formation of I-THMs (A) and I-HAAs (B) during chloramination of IPM with presence of ZVI. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.04$ mM, $[\text{IPM}]_0 = 10$ μM , $[\text{DOC}]_0 = 2.0$ mg L^{-1} , $[\text{ZVI}]_0 = 5.0$ g L^{-1} , 25 $^\circ\text{C}$, reaction time = 72 h. Error bars represent the 95% confidence interval.

formed, respectively, indicating that I-DBPs could form in real drinking water containing IPM during chloramination. Overall, the DOC-normalized total yield of I-DBPs in the four real waters followed the descending order of GW-raw > GW-filtered > SW-raw > SW-filtered, which may be attributed to their different contents of organic matter. The specific ultraviolet absorbance at 254 nm (SUVA_{254}) is widely used as an indicator of aromatic content and DBPs formation potential of NOM. The higher SUVA_{254} values of SW-raw and SW-filtered samples indicated their higher aromatic content than those of GW-raw and GW-filtered samples. In this study, it appears that low- SUVA_{254} NOM form more I-DBPs than high- SUVA_{254} NOM during chloramination, consistent with previous results (Jones et al., 2012; Chu et al., 2016b).

Note that although the I-DBPs formation amounts after filtration were reduced by 20.4% and 16.8% for the GW-raw and SW-raw samples, respectively, 7.1 and 3.6 $\mu\text{g mg}^{-1}$ I-DBPs were still formed from the GW-filtered and SW-filtered after 72 h. The insufficient removals of IPM and NOM during drinking water treatment processes would provide the opportunity for the coexistence of disinfectant (NH_2Cl), NOM and IPM in the distribution process. Then the released I^- by deiodination of IPM may promote the toxic I-DBPs formation during chloramination. Apart from the ZVI, various iron corrosion products including goethite, lepidocrocite, hematite, and magnetite may exist in iron distribution pipes (Yang et al., 2012) and impact the formation and transformation of I-DBPs, which needs a further research.

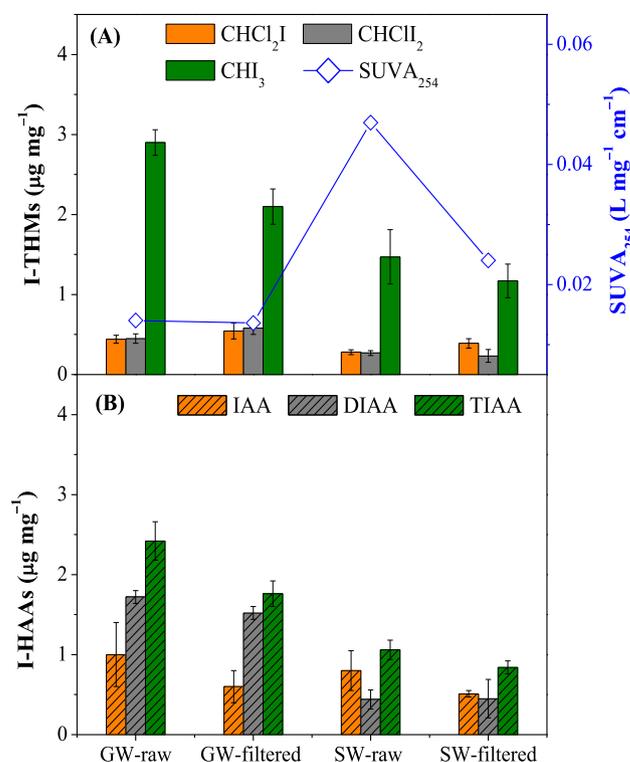


Fig. 7. Effect of ZVI on formation of I-THMs (A) and I-HAAs (B) in different water sample sources during chloramination of IPM. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.04$ mM, $[\text{IPM}]_0 = 500$ $\mu\text{g L}^{-1}$, $[\text{ZVI}]_0 = 5.0$ g L^{-1} , 25 $^\circ\text{C}$, reaction time = 72 h. Error bars represent the 95% confidence interval.

4. Conclusions

Based on the experimental results, the following conclusions can be drawn:

- ZVI could transform organic IPM into inorganic I^- and the transformation of IPM exhibited a pseudo-first-order kinetics.
- Acidic circumstance, SO_4^{2-} , Cl^- and monochloramine could promote the transformation of IPM by ZVI, while SiO_3^{2-} inhibited the transformation.
- Deiodination of IPM by ZVI shifted the formed dominant I-THMs and I-HAAs from CHCl_2I and iodoacetic acid to CHI_3 and triiodoacetic acid, respectively.
- Deiodination of IPM by ZVI increased I-DBPs formation amounts by 6.0 folds after 72 h and maximum formation of I-DBPs occurred at pH 5.0.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2017.11.032>.

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