



# Mechanism and kinetics of halogenated compound removal by metallic iron: Transport in solution, diffusion and reduction within corrosion films



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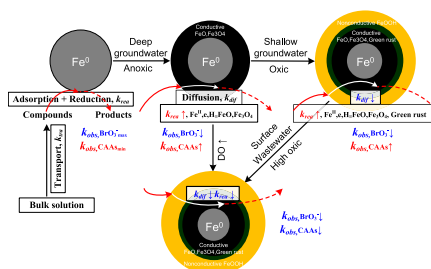
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## HIGHLIGHTS

- A kinetic model including  $k_{obs}$ ,  $k_{tra}$ ,  $k_{dif}$  and  $k_{rea}$  was proposed to elucidate the role of corrosion films.
- The trends of  $k_{obs}$ ,  $k_{tra}$ ,  $k_{dif}$  and  $k_{rea}$  values varied with the reactant species, operation time and O<sub>2</sub> content were explored.
- The effects of corrosion films on  $k_{dif}$  and  $k_{rea}$  values were responsible for the variation of  $k_{obs}$  value.
- Various product compositions were probably attributed to mass diffusion.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A detailed kinetic model comprised of mass transport ( $k_{tra}$ ), pore diffusion ( $k_{dif}$ ), adsorption and reduction reaction ( $k_{rea}$ ), was developed to quantitatively evaluate the effect of corrosion films on the removal rate ( $k_{obs}$ ) of halogenated compounds by metallic iron. Different corrosion conditions were controlled by adjusting the iron aging time (0 or 1 yr) and dissolved oxygen concentration (0–7.09 mg/L DO). The  $k_{obs}$  values for bromate, mono-, di- and tri-chloroacetic acids (BrO<sub>3</sub><sup>-</sup>, MCAA, DCAA and TCAA) were 0.41–7.06, 0–0.16, 0.01–0.53, 0.10–0.73 h<sup>-1</sup>, with  $k_{tra}$  values at 13.32, 12.12, 11.04 and 10.20 h<sup>-1</sup>,  $k_{dif}$  values at 0.42–5.82, 0.36–5.04, 0.30–4.50, 0.30–3.90 h<sup>-1</sup>, and  $k_{rea}$  values at 14.94–421.18, 0–0.19, 0.01–1.30, 0.10–3.98 h<sup>-1</sup>, respectively. The variation of  $k_{obs}$  value with reaction conditions depended on the reactant species, while those of  $k_{tra}$ ,  $k_{dif}$  and  $k_{rea}$  values were irrelevant to the species. The effects of corrosion films on  $k_{dif}$  and  $k_{rea}$  values were responsible for the variation of  $k_{obs}$  value for halogenated compounds. For a mass-transfer-limited halogenated compound such as BrO<sub>3</sub><sup>-</sup>, an often-neglected  $k_{dif}$  value primarily determined its  $k_{obs}$  value when pore diffusion was the rate-limiting step of its removal. In addition, the value of  $k_{dif}$  might influence product composition during a consecutive dechlorination, such as for TCAA and DCAA. For a reaction-controlled compound such as MCAA, an increased  $k_{rea}$  value was achieved under low oxidic conditions, which was favorable to improve its  $k_{obs}$  value. The proposed model has a potential in predicting the removal rate of halogenated compounds by metallic iron under various conditions.

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## 1. Introduction

Over the last two decades, zero-valent iron ( $\text{Fe}^0$ ) and  $\text{Fe}^0$ -based particles have been widely used to remove a wide range of compounds, such as halogenated organics, nitrogen-containing organics, inorganic anions, metal ions and pathogenic microorganisms (Cundy et al., 2008; Gunawardana et al., 2011; Li et al., 2006; Scott et al., 2011). Moreover, hundreds of  $\text{Fe}^0$ -based permeable reactive barriers (PRBs) have been built for in-situ remediation of contaminated soil, groundwater and wastewater (Chen et al., 2011; Fu et al., 2014; Jeon et al., 2011; Ma and Zhang, 2008; Obiri-Nyarko et al., 2014). At the beginning, the mechanism of reducible species removed by  $\text{Fe}^0$  was widely accepted as an electrochemical or a chemical reduction process, and  $\text{Fe}^0$ , soluble ferrous ion ( $\text{Fe}^{2+}$ ) and hydrogen gas ( $\text{H}_2$ ) were the main reducing agents (Fu et al., 2014; Matheson and Tratnyek, 1994). Subsequently, the successful removal of some unreducible species, including methylene blue, zinc ions, bacteria and viruses, called attention to the importance of adsorption, precipitation and coprecipitation (Batkou et al., 2013; Noubactep, 2010; Shi et al., 2012; You et al., 2005). It was attributed to continuously generated and transformed iron corrosion products. Usually, these products at the surface of  $\text{Fe}^0$  in reduction reaction were served as physical barriers, semiconductors or coordinating surfaces (Sarin et al., 2004a; Scherer et al., 1998; Yan et al., 2010). The enhancement on reduction reactivity of iron was reported with coexisting  $\text{Fe}^{2+}$  or iron mineral (i.e. magnetite, green rust, pyrite or ferric hydroxide) (Cho et al., 2010; Coelho et al., 2008; Huang and Zhang, 2006; Huang et al., 2012, 2013; Kim et al., 2013; Mak et al., 2011; Song et al., 2013). The structural and surface-bound divalent irons ( $\text{Fe}^{\text{II}}$ ) were found as powerful reductants ( $-0.65$ – $-0.34$  V) (Haderlein and Pecher, 1998; Noubactep, 2008, 2009; White and Peterson, 1996). In general, the effect of in-situ formed iron corrosion products on the removal efficiency of involved species was inhibition or promotion. The influence of corrosion products on the removal process, especially on the rates of mass transfer and reduction reaction, was rarely investigated (Noubactep, 2010; Noubactep et al., 2010; Scherer et al., 2001; Sun et al., 2016).

The removal process by  $\text{Fe}^0$  particles involved the transfer of electrons usually occurred in the solid-liquid interface. This whole process was comprised of a series of steps, including the transport of the oxidizing species (i.e.  $\text{O}_2$ ,  $\text{H}^+$  and reducible compounds) from bulk solution to the surface of  $\text{Fe}^0$  particles, the reaction between  $\text{Fe}^0$  and the oxidizing species, as well as the transport of products away from the  $\text{Fe}^0$  particles (Guan et al., 2015). The pseudo-first-order kinetic model was widely used to quantify observed heterogeneous reaction rates (Alowitz and Scherer, 2002; Johnson et al., 1996; Zhuang et al., 2012). Although considering the mass transport in solution and reduction at the surface, it was insufficient to account for declining rate constants with increasing initial concentration of reactants (Li and Farrell, 2000; Miehr et al., 2004). Under this condition, the competition for reactive sites among involved compounds was taken into account. The mixed-order kinetic model and the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model were developed to combine the competitive adsorption and reduction reaction steps (Arnold and Roberts, 2000; Fan et al., 2009; Venkatapathy et al., 2002; Wang and Zhu, 2010; Wust et al., 1999; Zhang et al., 2004). As mentioned above, the role of corrosion products in the existing physical and mathematic models was intentionally ignored regardless of the known core-shell structure of iron corrosion (Sarin et al., 2004a; Scherer et al., 1998; Sun et al., 2016; Yan et al., 2010). In fact, the continuous reduction at the fresh  $\text{Fe}^0$  surface was nonrealistic since these reactive sites would be covered with corrosion products/films after immersion in water for a period of time (Noubactep, 2008).

Moreover, the structure (i.e. composition, thickness and porosity) of the corrosion films varied with reaction conditions would influence mass transfer from bulk solution to reactive sites. There was a difference in the concentration of a compound between the fluid at the external surface of iron particles and the fluid in the internal pores of corrosion films. Compared to the mass transport in bulk solution driven by mechanical mixing, the mass transport in corrosion pores was essentially governed by molecular diffusion at coefficients of  $10^{-12}$ – $10^{-16}$   $\text{cm}^2/\text{s}$  (Crittenden et al., 2012; Guan et al., 2015; Noubactep, 2008; White et al., 1994). The pore diffusion rate in the corrosion films was likely to control the removal rate of halogenated compounds (Tang et al., 2015).

Halogenated compounds were widely detected in industrial wastewater, natural water and drinking water, possible for the difficulty of biological degradation or chemical oxidation. Some of these compounds were highly toxic to human health and the environment.  $\text{Fe}^0$  was regarded as a cost-effective technology for the removal of halogenated compounds (Fu et al., 2014). In order to quantitatively describe the effect of corrosion films on the removal rate of halogenated compounds by metallic iron, a detailed kinetic model was proposed and then confirmed in longitudinally mixed batch reactors in this study. Various corrosion conditions were controlled by adjusting the aging time of iron (0 or 1 year) and dissolved oxygen concentration (0–7.09 mg/L DO) (Sarin et al., 2004a, 2004b; Stratmann and Muller, 1994; Zhang and Huang, 2006). Disinfection by-products (DBPs) as unintended compounds formed in drinking water disinfection posed a potential health risk to water consumers (Krasner et al., 1989). Emerging brominated and iodinated DBPs were significantly more cytotoxic and genotoxic than the chlorinated DBPs (Richardson et al., 2007; Ding et al., 2013; Gong and Zhang, 2015). So far, approximate 800 compounds were detected as DBPs (Yang and Zhang, 2016). Trihalomethanes (THMs), haloacetic acids (HAAs), bromate ( $\text{BrO}_3^-$ ) and chlorite were regulated in Disinfectants/Disinfection By-Products Rule by the US Environmental Protection Agency (USEPA, 2006). Reactions of DBPs with  $\text{Fe}^0$  might have important implications for understanding the fate of DBPs in water distribution systems, which primarily consisted of cast iron piping (Hozalski et al., 2001). Because of a need to periodically refresh the reactor headspace to maintain a stable DO value, non-volatile regulated DBPs,  $\text{BrO}_3^-$  (reduction pathway:  $\text{BrO}_3^- \rightarrow \text{Br}^-$ , Xie and Shang, 2007) and chloroacetic acids (CAAs) (reduction pathway: TCAA (trichloroacetic acid)  $\rightarrow$  DCAA (dichloroacetic acid)  $\rightarrow$  MCAA (monochloroacetic acid)  $\rightarrow$  AA (acetic acid), Zhang et al., 2004) were selected as the model compounds. The detailed kinetics and rate-determining steps of the removals of  $\text{BrO}_3^-$  and CAAs were also explored in the iron-water systems.

## 2. Proposed physical and mathematic kinetic model

According to our previous study (Tang et al., 2015), the physical process of halogenated compounds removed by iron with/without corrosion films was reproduced in Fig. 1. This whole process typically involved a series of steps, including (I) the mass transport of halogenated compounds from bulk solution to the surface of iron particles, (II) the pore diffusion of the compounds from the external surface to the reactive interface, (III) the competition adsorption of the compounds on reactive sites, (IV) the reduction reaction between reducing agents and the compounds, as well as (V) the desorption and transfer (converse diffusion and transport) of reduction products away from the iron particles. Only for a short period of time after acid washing, step II could be neglected. After that, the corrosion films were formed on the surface of  $\text{Fe}^0$ . These films were potentially comprised of ferrous oxide, magnetite, green rust, lepidocrocite and amorphous iron hydroxide (Fan et al., 2009;

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