TECH NOTE

Ferrates(Fe^{VI} , Fe^{V} , and Fe^{IV}) Oxidation of Iodide: Formation of Triiodide

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ABSTRACT

The presence of iodide (I^-) in water during disinfection and oxidative treatment of water is a potential health concern because of the formation of iodinated disinfection by-products (DBPs), which may be more toxic than chlorinated DBPs. The kinetics of the oxidation of I^- by a greener oxidant, ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) was determined as a function of pH. The second-order rate constants (k , $M^{-1}s^{-1}$) decreased from $3.9 \times 10^4 M^{-1}s^{-1}$ at pH 5.0 to $1.2 \times 10^1 M^{-1}s^{-1}$ at pH 10.3. The kinetics results could be described by the reactivity of monoprotonated species of Fe(VI) ($HFe^{VI}O_4^-$) with I^- . In excess I^- concentration, triiodide (I_3^-) was formed and the stoichiometry of $\sim 1:1$ ($[Fe(VI)]:[I_3^-]$) was found in both acidic and basic pH. Ferrate(V) ($Fe^VO_4^{3-}$, Fe(V)) and ferrate(IV) ($Fe^{IV}O_4^{4-}$, Fe(IV)) also showed the formation of I_3^- in presence of excess I^- . A mechanism of the formation of I_3^- is proposed, which is consistent with the observed stoichiometry of 1:1. The oxidative treatment of I^- in water will be rapid ($t_{1/2} = 0.6$ s at pH 7.0 using $10 \text{ mg L}^{-1} K_2FeO_4$). The implications of the results and their comparison with the oxidation of I^- by conventional disinfectants/oxidants in water treatment are briefly discussed.

Keywords: Ferrate; iodide; oxidation; disinfection by-products; mechanism

1. Introduction

Three forms of iodine are usually present in natural waters, iodide (I^-), iodate (IO_3^-), and organic-iodine (Liu, et al., 2014). The main species are I^- and IO_3^- in fresh water and seawater, respectively. Organic-iodine in natural waters is usually of minor relevance (Gong and Zhang, 2013). Levels of total iodine are highly variable, and are commonly higher in seawater than in fresh surface water ($60 \mu\text{g L}^{-1}$ versus $0.5 - 20 \mu\text{g L}^{-1}$, respectively) (Tsunogai and Henmi, 1971; Moran, et al., 2002). A range of I^- concentrations from 0.4 to $104 \mu\text{g L}^{-1}$ has been found in water resources of Canada and United States (Richardson, et al., 2008). There is concern about I^- in source waters for drinking water because of its role in the formation of iodinated disinfection byproducts (DBPs) during disinfection and oxidative treatment (Zhang, et al., 2015). Iodinated DBPs are among the most toxic DBPs identified in drinking water (Richardson, et al., 2007).

Chlorine, chloramine, chlorine dioxide, and ozone are applied in oxidative treatment, which can easily oxidize I^- in fresh water at neutral pH (Nagy, et al., 1988; Hua, et al., 2006; Allard, et al., 2013; Ye, et al., 2013; Zhang, et al., 2015). Lead oxide, manganese oxide, and permanganate can also oxidize I^- (Ye, et al., 2013). Oxidation of I^- generally leads to the formation of hypiodous acid (HOI), which slowly degrades to I^- and iodate (IO_3^-) (Bichsel and Von Gunten, 2000). Iodate is a preferable byproduct due to its inertness and lacks of non-toxicity (Bichsel and von Gunten, 1999). However, there is a possibility that the formed HOI reacts with other components of water sources (e.g. bromide and natural organic matter) to produce iodinated-DBPs (Richardson and Ternes, 2014). The present paper focuses on studying the oxidation of iodide by iron in high oxidation states, called ferrates ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, $\text{Fe}^{\text{V}}\text{O}_4^{3-}$, and $\text{Fe}^{\text{IV}}\text{O}_4^{4-}$). Ferrates are environmentally-friendly oxidants and their effectiveness in removing emerging contaminants has been demonstrated (Jiang, 2014;

Karlesa, et al., 2014; Prucek, et al., 2015). There have also been found to minimize the formation of DBPs (Gan, et al., 2015).

The present study is the first report of kinetics measurements for the oxidation of I^- by Fe(VI) in the acidic medium. Other studies on ferrates (Fe(V) and Fe(IV)) are very limited (Yates, et al., 2014) and the current paper adds new information on these unusual high-valent iron species. The aims of the paper are to: (i) measure the kinetics of oxidation of I^- by Fe(VI) over a wide pH range to characterize the rate constants over a range of pH values, (ii) comprehend the kinetic behavior of I^- oxidation by applying the kinetic model of species-specific reactions, (iii) determine the stoichiometry of ferrates (Fe^{VI} , Fe^V , and Fe^{IV}) with I^- to understand the mechanism of oxidation of I^- by Fe(VI), and (iv) compare the oxidation of I^- by Fe(VI) with I^- oxidation by other conventional oxidants (chlorine, chloramine, chlorine dioxide, ozone, and permanganate) in order to learn the role, if any, of Fe(VI) in generating DBPs in water treatment processes.

2. Materials and methods

2.1 Chemicals

Potassium iodide (KI), sodium hydrogen phosphate (Na_2HPO_4), and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) were purchased from either Fisher Scientific (Austin, TX, USA) or Sigma-Aldrich (St. Louis, MO, USA). Solid potassium ferrate (K_2FeO_4) was synthesized using a wet chemical method and the purity obtained was > 98% (Luo, et al., 2011). Solid salts of Fe(V) (K_3FeO_4) and Fe(IV) (Na_4FeO_4) were synthesized by thermal techniques; the purities were tested by ^{57}Fe Mössbauer spectroscopy (Sharma, et al., 2015). Solid K_3FeO_4 had an impurity of Fe(VI) and the composition was 75 % Fe(V) and 25 % Fe(VI) whereas Na_4FeO_4 was highly pure (Sharma, et al., 2015). A solution of Fe(VI) was prepared by putting solid crystals of K_2FeO_4 into 1 mM borate/5 mM Na_2HPO_4 solutions at pH 9.0. The concentration

of Fe(VI) in solution was confirmed by measuring its absorbance at 510 nm ($\epsilon_{510\text{ nm}} = 1150\text{ M}^{-1}\text{cm}^{-1}$) (Luo, et al., 2011). A UV-visible spectrophotometer (Agilent 8453, Santa Cruz, CA, USA) was used to collect absorbance measurements. Solutions of iodide were prepared by dissolving KI into 0.01 M phosphate solution and the pHs of the solutions were adjusted using either sodium hydroxide or phosphoric acid. All solutions were prepared using de-ionized water that was previously passed through 18 M Ω cm Millipore water purification system (Waters Alliance, Milford, MA, USA).

2.2. Kinetics experiments

A stopped-flow spectrophotometer (SX-20 MV, Applied Photophysics, Surrey, UK), equipped with UV-Vis and photodiode array detector was used to study the reaction between Fe(VI) and iodide. Pseudo-order conditions were applied in which the concentrations of iodide were higher than Fe(VI) concentration. A wavelength of 510 nm was used to collect kinetic traces and the data were analyzed using the non-linear least-square algorithm of the SX-20MV Global software (Applied Photophysics, Surrey, UK). Six replicate runs were carried out to calculate averaged rate constants. The pseudo-order rate constants for the reaction between Fe(VI) and iodide were obtained by subtracting the observed rate constants from the Fe(VI) decay without iodide at each pH (Anquandah, et al., 2013).

2.3. Product studies

The stoichiometric experiments at pH 6.0 and 9.0 at 25 °C were carried out by mixing both solutions (10 mL each) of Fe(VI) and iodide. The concentrations of iodide were varied while keeping the concentration of Fe(VI) at $5.0 \times 10^{-4}\text{ M}$ in 1 mM borate/5 mM phosphate (pH 9.0) to attain different ratios of iodide to Fe(VI). The pH of the iodide solution in phosphate buffer (0.01 M) was changed to achieve different pH of the mixed solutions. After

no residual Fe(VI) was observed (i.e. the reaction was completed), the spectra of the mixed solution was collected. Spectral measurements of the yellowish color of the mixed solution for formed I_3^- were performed on an UV-visible spectrophotometer. A quartz cell was used in which the pathlength was 1.0 cm. In cases of the reactions of Fe(V) and Fe(IV) at different pH, the experiments were performed in a glove box with dry N_2 atmosphere, in order to prevent oxidation of ferrates by ambient air humidity or the presence of oxygen. Solid compounds of Fe(V) and Fe(IV) were directly added to the iodide solution and the spectra of observed yellowish color were measured.

Formation of dissolved oxygen during the reaction of Fe(VI) and iodide was determined using an oxygen meter (Mettler Toledo, Ohio, USA). In this set of experiments, both solutions were first purged with nitrogen to achieve anaerobic conditions before mixing. Reactions were instantaneous and oxygen measurements were performed immediately of the mixed solutions.

3. Results and Discussions

3.1. Fe(VI) kinetic study

Initially, the reaction of Fe(VI) with I^- under pseudo first-order conditions was monitored at pH 6.0 by following the absorbance of Fe(VI) as a function of time. Decreases in absorbance due to the decay of Fe(VI) fit nicely to single-exponential decay. Plots of observed pseudo first-order rate constants (k_1) showed linear relationships with concentrations of I^- in ($r^2 = 0.99$) (e.g. [Fig. SM-1](#)). Plots of $\log k_1$ versus $\log[I^-]$ gave a first-order term with respect to the concentration of I^- . Similar results were obtained at other acidic pH range (5.0, 5.5, 6.7, and 7.0). Significantly, first-order terms with respect to $[Fe(VI)]$ and $[I^-]$ are in

agreement with the results obtained earlier in the alkaline medium (Sharma, 2010). The rate law in the entire pH range can be written as:

$$-d[\text{Fe(VI)}]/dt = k[\text{Fe(VI)}]_{\text{tot}}[\text{I}^-] \quad (1)$$

The second-order rate constants as a function of the pH are shown in Fig. 1. The rate of the reaction decreased with an increase in pH in alkaline medium, while only a small variation was seen in the acidic pH range (Fig. 1). Results in the alkaline pH range are similar to previous studies (Noorhasan, et al., 2010; Sharma, et al., 2013), but the trend in the acidic medium is unexpected. The protonation of Fe(VI) increases when the pH is lowered, and this generally increases the reactivity. Iodide ion does not have any protonation involvement in the pH range of the study; therefore, the pH dependence is solely related to the protonation of Fe(VI). Fe(VI) is a stronger oxidant upon protonation (Kim, et al., 2015), and usually the apparent reaction rate constant increases at lower pH value. Therefore, the reaction rate constant of I⁻ with Fe(VI) was expected to keep increasing as the pH decreased.

These kinetic measurements at different pH values were evaluated using the species of Fe(VI) over the entire pH range ($\text{H}_3\text{Fe}^{\text{VI}}\text{O}_4^+ \rightleftharpoons \text{H}^+ + \text{H}_2\text{Fe}^{\text{VI}}\text{O}_4$, $\text{p}K_{\text{a1}} = 1.9$; $\text{H}_2\text{Fe}^{\text{VI}}\text{O}_4 \rightleftharpoons \text{H}^+ + \text{HFe}^{\text{VI}}\text{O}_4^-$, $\text{p}K_{\text{a2}} = 3.5$; $\text{HFe}^{\text{VI}}\text{O}_4^- \rightleftharpoons \text{H}^+ + \text{Fe}^{\text{VI}}\text{O}_4^{2-}$, $\text{p}K_{\text{a3}} = 7.23$) (Sharma, et al., 2001). The following model was used to interpret the data in Fig. 1 (eq. 2):

$$k[\text{Fe(VI)}]_{\text{Tot}}[\text{I}^-] = \sum_{i=1,2,3,4} k_i \alpha_i [\text{Fe(VI)}]_{\text{Tot}}[\text{I}^-] \quad (2)$$

where $[\text{Fe(VI)}]_{\text{Tot}} = [\text{H}_3\text{Fe}^{\text{VI}}\text{O}_4^+] + [\text{H}_2\text{Fe}^{\text{VI}}\text{O}_4] + [\text{HFe}^{\text{VI}}\text{O}_4^-] + [\text{Fe}^{\text{VI}}\text{O}_4^{2-}]$. α_i represents the species distribution coefficients for Fe(VI), respectively, and i represents each of the four species of Fe(VI).

Initially, interpretation of kinetic data was conducted using the description given earlier in the previous study in alkaline medium which used the fraction of $\text{HFe}^{\text{VI}}\text{O}_4^-$ species ($\alpha(\text{HFeO}_4^-)$) (Sharma, 2010). As shown in Fig. 2A, a linear relationship between the apparent rate constant and $\alpha(\text{HFeO}_4^-)$ was determined; the slope of the linear regression line is the rate constant for the reaction between $\text{HFe}^{\text{VI}}\text{O}_4^-$ and I^- (eq 3).

The reaction (3) was then used to interpret the kinetic data in the acidic medium because $\text{HFe}^{\text{VI}}\text{O}_4^-$ species is the dominant species and fractions of $\text{H}_3\text{Fe}^{\text{VI}}\text{O}_4^+$ and $\text{H}_2\text{Fe}^{\text{VI}}\text{O}_4$ were not significant in pH range from 5.0 and 7.0. Significantly, the value of k_3 did not fit the experimental data in the acidic pH range (see dashed line of Fig. 1).

Next, kinetic data in acidic medium were fitted independently using the $\alpha(\text{HFeO}_4^-)$. As shown in Fig. 2B, the rate constants could be fit nicely with the fractions of $\text{HFe}^{\text{VI}}\text{O}_4^-$ (a solid line in Fig. 1), however, the value of the slope $(4.0 \pm 0.6) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ differed from that obtained in basic medium. This was puzzling because in both acidic and basic medium, the reactants were the same (i.e. $\text{HFe}^{\text{VI}}\text{O}_4^-$ and I^-). This led us to hypothesize that the oxidation of I^- might produce different products during the initial steps in basic and acid solutions. In the basic medium, the initial step of the oxidation of I^- by Fe(VI) was the formation of $\text{I}^\bullet$, based on the relationship between the linear relationship between rate constants and redox potentials for one-electron transfer (1-e^-) of numerous inorganic contaminants (eq. 4) (Sharma, 2010).

$$\log k (1\text{-e}^-) = 6.39(\pm 0.05) - 1.83E_{(1)}^0(\pm 0.04) \quad (4)$$

Therefore, the first step of the mechanism of reaction (3) could be written as reaction (5).

The redox potential, $E_{(1)}^0$, of 1.27 V ($\text{I}^\bullet/\text{I}^-$) could predict the value of k_3 in a basic medium (Sharma, 2010). The slope of Fig. 2B in an acidic medium was used to calculate redox $E_{(1)}^0$ in order to predict different mechanism step from reaction (5) in the acidic medium. The

value of $E_{(1)}^0$ in acidic medium was obtained as 0.97 (± 0.05) V; which is in reasonable agreement with a reported range of 0.98-1.13 V for the $I_2^{\bullet-}/2I^-$ redox pair (Wardman, 1989). Thus reaction (6) is proposed as the first step of the mechanism in the studied acidic pH range.

More discussion on the mechanism of oxidation of I^- by Fe(VI) is given in section 3.3.

3.2. Formation of triiodide

Initially, solutions of 1.0×10^{-4} M Fe(VI) and 0.01 M I^- were mixed at pH 9.0 and spectrum was measured. The pink color (or characteristic spectra of Fe(VI) with a maxima at 510 nm) rapidly disappeared and a concomitant growth of a new spectra with a maxima at ~ 351 nm appeared, which was assigned to the triiodide (I_3^-) species (Lam, et al., 2008). Similar mixing of solutions was carried out at various concentration ratios of I^- to Fe(VI) ($[I^-]:[Fe(VI)]$), which again showed the formation of I_3^- . However, the growth of the peaks at 351 nm varied with the ratios. An extinction coefficient for I_3^- ($\epsilon_{351\text{ nm}} = 2.97 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) (Luo, et al., 2011) was used to calculate the concentrations of I_3^- in different mixed solutions. The results of the ratios of the formation of I_3^- and Fe(VI) in the reaction solution ($[I_3^-]/[Fe(VI)]$) were plotted as a function of ($[I^-]:[Fe(VI)]$) and are shown in Fig. 3. Similar experiments were performed in acidic solution (pH 6.0) and results are also shown in Fig. 3. The formation of I_3^- increased with increasing ratios of $[I^-]:[Fe(VI)]$ and then became constant at $[I^-]:[Fe(VI)] \geq 2000$; the limiting stoichiometry was 1:1.

A similar trend of the formation of I_3^- was found at pH 6.0 and the limiting stoichiometry was somewhat higher than 1:1; perhaps similar to pH 9.0 within the experimental error of the measurements (Fig. 3). The Mössbauer spectroscopic

measurements at pH 6.0 and 9.0 of final products of the reactions showed that the reduced iron species from Fe^{VI} was Fe^{III}. Stoichiometric results may be presented by eq. 7.

The formation of I₃⁻ was also sought in the reactions of Fe^V and Fe^{IV} with I⁻. High concentrations of I⁻ were used to ensure that these unstable species react with I⁻ rather self-decomposed (Sharma, et al., 2008). The rate constants for the self-decomposition are high ($2k \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and decay on a millisecond or less time scale. Reactions of Fe^V and Fe^{IV} with I⁻ resulted in the characteristic peaks of the formation of I₃⁻ (Fig. 4). Significantly, growths of the I₃⁻ formation were less in basic medium compared to acidic and nearly neutral solutions (Fig. 4). This variation in I₃⁻ formation with pH suggests that the reaction of Fe(V)/Fe(IV) with I⁻ was more pronounced in acidic solution than at pH 10.6 (or 9.0). This is consistent with an increase in reactivity of Fe^V and Fe^{IV} species with decreasing pH (Bielski, et al., 1994). Furthermore, self-decomposition of Fe^V/Fe^{IV} species were also simultaneously occurring; their rates also increase with decrease in pH. Results of Fig. 4 at different pH values indicate differences in rates between the reactions of ferrates with I⁻, and self-decomposition were greater in acidic pH than in basic pH.

3.3. Plausible mechanism

The reactions that may occur in the oxidation of I⁻ by Fe(VI) are given in Table 1. The initial oxidation of I⁻ by Fe(VI) is an one-electron step that resulted in Fe(V) and iodide radical (I[•]) (reaction R1). Similar one-electron transfer steps may also be possible for Fe^V and Fe^{IV} species (reactions R2 and R3). One-electron transfer steps, given in reactions R1-R3, are similar to the oxidation of cyanide by ferrates (Sharma, et al., 2008). Based on the kinetics measurements, the possibility of the formation of iodine radical anion (I₂^{•-}) exists, could possibly be formed by reactions R4-R6. The I₂^{•-} is considered as a reducing radical,

which has been found to convert complexes of Fe(III) to Fe(II) (Wang and Stanbury, 2006); therefore reduction of ferrates by this radical is proposed (reactions R7 and R8). The possible reactions among iodine species are presented as reactions I1-I5. The formation of I_2 may occur from the iodide radical (I1). If iodide radical reacted with iodide, it would yield $I_2^{\bullet-}$ (reaction I2). The formation of I_3^- could be possible from three reactions (I3-I5). If intermediate ferrate species (Fe^V and Fe^{IV}) do not participate in reactions with iodine species, their self-decomposition would result in Fe(III) (reactions F1 and F2).

A combination of reactions in Table SM-1, given in Schemes S1-S5, may describe the stoichiometric results of 1:1 ($[Fe(VI)];[I_3^-]$) (see Fig. 3). Scheme S1 considers Fe(V), produced in an initial step, also further reacted with I^- through a one-electron transfer to give Fe(IV) and $I^{\bullet}$ (reactions R1 and R2). Reactions I1 and I2 subsequently followed to give I_3^- . In Scheme 1, Fe(IV) does not react with I^- and it decomposes to Fe(III), the experimentally observed reduced iron species of Fe(VI) (reaction F2). Overall, the combination of reactions R1, R2, I1, I3, and F2 give the stoichiometry of 1:1 between Fe(VI) and I_3^- . Variation in the stoichiometry of the formation of I_3^- at low reactant ratios of I^- to Fe(VI) indicates that involvement of Fe(V) happened only at high concentrations of I^- ($[I^-]/[Fe(VI)] > 1000$). A high concentrations of I^- ensured that reaction R2 occurred rather than self-decomposition of Fe(V) (reaction F1). This is also supported by the formation of I_3^- in the reaction of Fe(V) with I^- (see Fig. 4A). Without Fe(V) involvement, the stoichiometry would be less than 1:1, seen at low concentrations of I^- . Significantly, if Fe(IV) had reacted with I^- , the stoichiometry would be 2:3, which is in contrast with the observed stoichiometry (Scheme 2). Therefore, Fe(IV) did not participate in the reaction with I^- .

The observed stoichiometry of 1:1 may also be explained by the formation of the $I_2^{\bullet-}$ species (Scheme 3), a likely species in the acidic medium. A combination of reactions, R4, R5, R7, R8, I3, and F2 gave 1:1 stoichiometry between Fe(VI) and I_3^- (Fig. 3). Interestingly,

both the initial one-electron transfer species, $I^\bullet$ and $I_2^{\bullet-}$ from I^- , were able to describe the stoichiometry. Again, involvement of Fe^{IV} species in the reaction would produce a deviation from the observed stoichiometry (*Scheme S4*). Other possibility in which formed Fe^V and Fe^{IV} species subsequently reacted with $I_2^{\bullet-}$ resulted in different stoichiometry than 1:1 ($[Fe(VI)]:[I_3^-]$) (*Scheme S5*).

3.4. Implications in water treatment

A comparison of $Fe(VI)$ to oxidize I^- with other conventional oxidants is given in [Table 2](#) (Kumar, et al., 1986; Nagy, et al., 1988; Fábíán and Gordon, 1997; Bichsel and von Gunten, 1999). At a neutral pH, the reactivity of oxidants increased in order of $ClO_2 < NH_2Cl < HFe^{VI}O_4^- \sim HOCl < O_3$. The oxidation of I^- by ClO_2 occurred through an initial step of the formation of $I^\bullet$, similar to $Fe(VI)$. Other oxidants (ozone, chlorine, and chloramine) also reacted fast with I^- and the product was HOI ($HOI \rightleftharpoons H^+ + OI^-$; $pK_a = 10.4$ (Liu, et al., 2014). Under the conditions of treatment, HOI may go through different processes: (i) disproportionate to IO_3^- and I^- ($3HOI \rightarrow IO_3^- + 2I^- + 3H^+$, $k = 0.3 \text{ M}^{-1}\text{s}^{-1}$ (Bichsel and Von Gunten, 2000), (ii) reacts with oxidant to form IO_3^- , and (iii) react with natural organic matter, one of the main constituents of water, to produce iodinated DBPs. HOI may also react rapidly with O_3 and chlorine to form IO_3^- ($k(HOI + O_3) = 3.6 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and $k(HOI + HOCl) = 5.2 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$ (Liu, et al., 2014)). Therefore, formation of iodinated DBPs is less during ozonation and chlorination. Chloramine does not oxidize HOI (Bichsel and von Gunten, 1999), therefore, possibility of the formation of iodinated-DBPs exists from the reaction of HOI with natural organic matter during chloramination of I^- .

The rate constant for oxidizing I^- at pH 7.0 is $2.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, which gives a half-life of I^- as 0.6 s if 10 mg L^{-1} K_2FeO_4 dose is used. Therefore, removal of I^- by $Fe(VI)$ can be achieved rapidly. Oxidation of I^- by $Fe(VI)$ yields $I^\bullet$ or $I_2^{\bullet-}$ which would ultimately produce

I₂. In water, I₂ goes through equilibrium ($I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$; $K = 5 \times 10^{-10} \text{ M}^{-2}$ (Bichsel and Von Gunten, 2000)). The value of equilibrium constant suggests that I₂ will remain in the solution. The produced I₂ can rapidly react with I⁻ to yield stable I₃⁻ ($k = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton and Mulazzani, 2007)). Another possibility would be that I₂ reacts with organic matter present in water and generates iodinated-DBPs. This needs careful investigation to fully learn the formation of iodinated DBPs during oxidation of I⁻ by Fe(VI) in organic matter containing water.

4. Conclusion

The reaction between Fe(VI) and I⁻ followed second-order kinetics in both acidic and basic pH. The values of second-order rate constants decreased with increasing pH. The kinetic modelling involving the equilibrium species of Fe(VI) (HFe^{VI}O₄⁻) could describe the pH dependent behavior of the rate over the entire pH range. However different species, I[•] and I₂^{•-}, generated from the initial step of the oxidation of I⁻ in basic and acid solutions, respectively, were invoked to explain the kinetics as a function of pH. All ferrate species (Fe^{VI}, Fe^V, and Fe^{IV}) oxidized I⁻ to I₃⁻ species in the presence of excess I⁻. The proposed mechanism for the oxidation of I⁻ by Fe(VI) was in reasonable agreement with the observed stoichiometry of 1:1 ([Fe(VI)]:[I₃⁻]). Under excess I⁻ over Fe(VI), formed I₃⁻ may react with natural organic matter to yield iodinated disinfection by-products (I-DBPs). The role of oxidation of I⁻ by Fe(VI) under real water conditions containing natural organic matter in the generation of I-DBPs may be explored in future studies.

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Table 1. Possible reactions during the oxidation of I^- by Fe(VI) .

Reaction between ferrates and iodine species

Reactions of iodine species

Reactions of ferrates species

Table 2. Rate constants for the oxidation of I⁻ by Fe(VI) and other oxidants/disinfectants.

Oxidant Disinfectant	Rate Constant	Product	Reference
HFe ^{VI} O ₄ ⁻	$4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	I [•] /I ₂ ^{•-}	This study
ClO ₂	$1.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	I [•]	(Fábián and Gordon, 1997)
HOCl	$4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	HOI	(Nagy, et al., 1988)
NH ₂ Cl	$1.24 \times 10^{10} \times [\text{H}^+] \text{ M}^{-2} \text{ s}^{-1}$	HOI	(Kumar, et al., 1986)
O ₃	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	HOI	(Bichsel and von Gunten, 1999)

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457 **Fig. 1.** The apparent second-order rate constant ($k_{obs, M^{-1} s^{-1}}$) as a function of pH for the
 458 reaction between Fe(VI) and iodide at 25 °C (Reaction X considers reaction 5 as an initial step
 459 and Reaction Y considers reaction 6 as an initial step) (data in basic medium were taken from
 460 (Sharma, 2010).

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467 **Fig. 2.** Variation of apparent second-order rate constant ($k_{\text{obs}}, \text{M}^{-1} \text{s}^{-1}$) as a function of fractions
 468 of monoprotated Fe(VI) species. A-Basic pH and B-Acidic pH.

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473 **Fig. 3.** Stoichiometry of the reaction between Fe(VI) and iodide at pH 6.0 and 9.0
 474 (Experimental conditions: $\text{Fe(VI)} = 1.0 \times 10^{-4} \text{ M}$). Inset: Formation of triiodide (I_3^-) at pH
 475 9.0 (Experimental conditions $\text{Fe(VI)} = 1.0 \times 10^{-4} \text{ M}$ and $[\text{I}^-] = 1.0 \times 10^{-2} \text{ M}$).

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Fig. 4. Formation of triiodide (I_3^-) in the reactions of Fe(V) (A) and Fe(IV) (B) with iodide at different pH.

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