Oxidation of iodide and iodine on birnessite (δ-MnO_2) in the pH range 4 - 8

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Abstract

The oxidation of iodide by synthetic birnessite (δ-MnO_2) was studied in perchlorate media in the pH range 4 to 8. Iodine (I_2) was detected as an oxidation product that was subsequently further oxidised to iodate (IO_3^-). The third order rate constants, second order on iodide and first order on manganese oxide, determined by extraction of iodine in benzene decreased with increasing pH (6.3 – 7.5) from 1790 to 3.1 M^{-2} s^{-1}. Both iodine and iodate were found to adsorb significantly on birnessite with an adsorption capacity of 12.7 µM/g for iodate at pH 5.7. The rate of iodine oxidation by birnessite decreased with increasing ionic strength, which resulted in a lower rate of iodate formation. The production of iodine in iodide-containing waters in contact with manganese oxides may result in the formation of undesired iodinated organic compounds (taste and odor, toxicity) in natural and technical systems. The probability of the formation of such compounds is highest in the pH range 5 - 7.5. For pH < 5 iodine is quickly oxidized to iodate, a non-toxic and stable sink for iodine. At pH > 7.5, iodide is not oxidized to a significant extent.

Key words: Manganese dioxide, birnessite, iodide, iodine, iodate, kinetics, oxidation, adsorption

Introduction

Iodine species and their occurrence in aquatic systems

The complex chemistry of iodine in the environment is a result of its multiple oxidation states and of its biophilic character (for reviews see Fuge and Johnson (1986) and Wong (1991)). Iodine is mainly present in the environment as iodide I^- with oxidation state –I and iodate IO_3^- with oxidation state +V. A fraction of iodine is also present in the environment as iodoorganic compounds that are produced by microorganisms (Wong, 1991; Gschwend et al., 1985) or by chemical redox reactions (Keppler et al., 2000; Lin et al., 2008; Keppler et al., 2003; Zafiriou, 1975). Elemental iodine I_2 (oxidation state 0) and hypoiodous acid HOI (oxidation state +I) can also exist as reactive intermediates i.e. metastable species at low concentrations.

Iodine is found in seawater at a higher concentration than in any other environment. An average value of 58 µg/L is estimated for the total iodine concentration (Fuge and Johnson, 1986). In seawater iodine is mostly present as iodate. Iodide maxima and thus iodate minima are often found in surface waters (Wong, 1991). In contrast to seawater, iodine is present in freshwater mainly as iodide and at much lower concentrations (Smith and Butler, 1979). The concentration of total iodine is in the range of 0.5 – 20 µg/L in river waters (Fuge and Johnson, 1986) but concentrations up to 200 µg/L were analysed in a mineral water resulting of water infiltration in marine molasse (Bichsel and von Gunten, 1999a). Rainfall and seawater infiltration are also common sources of iodine in freshwaters. For these reasons, total iodine concentrations are higher in coastal areas.

Manganese speciation and reactivity

After iron, manganese is the second most common transition metal in the Earth's crust. The most extensive deposition of Mn oxides today occurs in the oceans as Mn nodules (Murray et al., 1984). In marine and freshwater environments, manganese is mainly present in its oxidation state

+IV (Murray et al., 1984; Zidenberg-Cherr and Keen, 1987). Manganese oxide minerals participate in a variety of chemical reactions involving both organic and inorganic compounds. This results in oxidation, reduction and scavenging (sorption, precipitation) processes. Manganese oxides have received considerable attention in environmental studies due to their ability to oxidize Co(II) to Co(III) (Manceau et al., 1997), Cr(III) to Cr(VI) (Guha et al., 2001; Johnson and Xyla, 1991; Negra et al., 2005), As(III) to As(V) (Scott and Morgan, 1995), Se(IV) to Se(VI) (Scott and Morgan, 1996) and S(-II) to S(0) (Yao and Millero, 1993). Based on these properties, manganese oxides are also used for the removal of iron and manganese (White and Asfar-Siddique, 1997) and arsenic (Scott and Morgan, 1995; Ouvrard et al., 2002) in water treatment.

Oxidation of iodide by MnO_2

The oxidation of iodide by manganese oxides is a well known reaction in acidic solution. This reaction is used for the analysis of oxygen according to the Winkler titration (Winkler, 1888). The Mn:O stoichiometry of manganese oxide is also determined by iodometric titration (Murray et al., 1984). The oxidation of iodide to iodine and/or iodate was already discussed in literature based on thermodynamic data (Anschutz et al., 2000). Truesdale et al. (2001) concluded that the oxidation of iodide to iodine is thermodynamically possible at pH below 6.5 – 7.0, depending on the concentrations of manganous ion and the I_2/I^- ratios. Similar considerations for the couple IO_3^-/I^- indicate that the oxidation of iodide to iodate by manganese oxide is unlikely at pH > 7.75 (Truesdale et al., 2001). The Table 1 gives the half reactions of interest with the corresponding $E_H°$ and $p\varepsilon°$ (log K). The Figure 1 illustrates the thermodynamic calculations based on the data given in Table 1. The evolution of Δlog K vs. pH for the reactions between iodine species and δMnO_2 confirms that iodide could be oxidised to iodate for pH < 7 and shows that the oxidation of iodide to iodine would be thermodynamically favoured compared to the oxidation of iodine to iodate.

Thus, reactive iodine species (i.e. HOI or I_2) can be present in aquatic environmental and technical systems when manganese oxides get in contact with iodide-containing waters at near neutral pH values. Iodine or hypoiodous acid can further react with natural organic matter to produce iodo-organic compounds (Bichsel and von Gunten, 2000). From a drinking water point of view, the formation of iodo-organic compounds such as iodo-trihalomethanes is of concern because these compounds lead to taste and odour problems (Bichsel and von Gunten, 2000) and are more toxic than the chlorinated and brominated analogues (Plewa et al., 2004). Iodoacetic acid, produced also through the reactions between NOM and reactive iodine species, has been shown to be highly cytotoxic and genotoxic and to cause developmental abnormalities in mouse embryos (Richardson et al., 2008).

The oxidation of iodide has been extensively investigated by (Bichsel and von Gunten, 1999b) in water treatment conditions using oxidants such as ozone, chlorine and chloramines , however, such studies have not been conducted with manganese oxides at near neutral pH.

The objective of this paper was to investigate the kinetics of the oxidation of iodide and iodine by manganese dioxide under different experimental conditions (pH, ionic strength, concentrations of manganese oxides, iodide and iodine). This allows assessing the potential of the MnO_2-I^- system to form undesired iodo-organic compounds.

Material and methods

Chemicals

Potassium iodide, iodine and potassium iodate were analytical grade (purity $\geq$ 99%) and purchased from Carlo Erba. Sodium perchlorate was purchased from Acros Organic (purity $\geq$

99%) and iodophenols were purchased from Sigma Aldrich (purity ≥ 98%). All solutions were prepared with ultra pure water produced from a Milli-Q water purification system (Millipore).

Mn dioxide (δ-MnO_2, similar to the naturally occurring birnessite) was synthesized according to the procedure given in Murray (1973) and concentrated to ~200 mM by centrifugation. The concentration of the stock δ-MnO_2 suspension was measured by the spectrophotometric determination of the manganous ion (Mn(II)) (Brewer and Spencer, 1971) after the total reduction of δ-MnO_2 by ascorbic acid. The stoichiometry of the manganese oxide particles, determined by a iodometric titration (Murray et al., 1984), was Mn:O = 1:1.89. The surface area of δ-MnO_2 particles was determined by BET analyses and was found to be 140 m^2/g. The experiments were performed with the same suspension of freshly prepared δ-MnO_2 for the entire duration of the study (4 months) and no significant change in δ-MnO_2 reactivity was observed.

The pKa_2 value (eq.1) of the MnO_2 sites was determined from a potentiometric titration in a 0.01 M KNO_3 solutions with 0.02 M HCl and 0.02 M NaOH. All operations were carried out under an atmosphere of argon to avoid contamination with carbon dioxide. The titrations were carried out in a 200 cm^3 reactor at 25.0 (±0.5°C). A $pKa_2 = 4.0$ was obtained by fitting the titration data. The pH_{zpc} of birnessite was determined by Murray (1973) as 2.25.

$$\equiv MnOH \rightleftharpoons \equiv MnO^- + H^+ \qquad Ka_2 \qquad (1)$$

The total sites concentration was determined from the acid-base titration to be 2.15 mM/g i.e. 18 sites/nm^2. A similar surface site density of 18 sites/nm^2 was reported for synthetic birnessite by Yao and Millero (1996).

An aqueous iodine stock solution (0.5 mM) was prepared by dissolving sublimated iodine powder in ultra pure water. The exact concentration was determined by spectrophotometric measurement at a wavelength of 460 nm ($\varepsilon = 746\ M^{-1}\ cm^{-1}$) using a 50 mm optical cell.

Experimental procedures

The experiments of iodide and iodine oxidation by δ-MnO_2 were performed in 100 cm^3 amber bottles in a thermostated room at 25°C. The δ-MnO_2 particles (1 to 100 mM) were maintained in suspension using a magnetic stir bar agitator at 300 rpm during the course of the experiment. The reaction was induced by the addition of a predetermined volume of an iodide (10 mM) or iodine (0.5 mM) stock solution. At given time intervals, samples were withdrawn with a 50 mL syringe and filtered through a 0.2 µm membrane filter (diameter 12 mm, regenerated cellulose, Sartorius) for iodate and iodine analysis. Prior to iodide/iodine addition the pH was initially adjusted with 0.01 N NaOH and 0.01 N perchloric acid addition and ionic strength was fixed with $NaClO_4$ (0.1 mM to 10 mM). The solutions were not buffered to avoid interfering adsorption on manganese oxides or possible reactions between reactive iodine species and organic buffers. The pH values were monitored during the experiments. The oxidation of iodide and the formation of reactive iodine species and iodate were studied for different concentrations of iodide (5 µM – 100 µM), δ-MnO_2 (1 mM – 100 mM) and in the pH range 4 to 8.

The oxidation of iodide was also studied in the presence of benzene which was used to quickly extract iodine produced during the experiment. A blank experiment with iodine confirmed that extraction was quantitative. The experiments were carried out with 20 mL of an aqueous δ-MnO_2 suspension and 20 mL of benzene. The aqueous and the organic phases were separated at different time intervals and filtered through 0.2 µm membrane filter prior to iodide (aqueous phase) and iodine (organic phase) analysis. For both aqueous and organic phases, the filtration procedure did not cause any loss of iodine species.

Adsorption isotherms of iodate were obtained in perchlorate media at pH 5.7 by varying [IO_3^-] from 1 µM to 100 µM for [δMnO_2] = 10 mM and for a contact time of 24 hours. Preliminary experiments showed that the equilibrium is reached within 10 minutes.

Analytical methods

Iodide analyses were conducted with an iodide sensitive electrode (Orion 6-53 BN Thermo Electro Corporation) after filtration of the δ-MnO_2 suspension. There was no interference with iodate or elemental iodine.

Reactive iodine species (sum of I_2 and HOI) in aqueous solution were quenched with phenol and analyzed as iodophenols by HPLC. Phenol (200 µM) was added to the sample to transform iodine to iodophenols. Phenol reacts quickly and quantitatively with iodine (Bichsel and von Gunten, 2000). Both p-iodophenol and o-iodophenol were formed with an extent ratio of approximately 15:1. Because phenol was present in high excess, the formation of di- or triiodophenols was not observed. The two iodophenols were quantified relative to o- and p-iodophenol standard solutions. The iodine concentration was calculated as the sum of the two iodophenols. The HPLC separation was done on a Nucleosil 103-5 C18 column with an eluent consisting of 50% methanol, 49.85% water, and 0.15% acetic acid. The UV detection at 231 nm yielded a detection limit of 0.3 µg I/L (Bichsel and von Gunten, 2000).

Iodate analysis were performed according to the method described by Salhi and von Gunten (1999). A Dionex® AS19 column and AG19 guard column with 25 - 100 mM NaOH eluent were used. The injection volume was reduced to 100 µl to limit the response of perchlorate. The detection limit was 20 nM with a standard deviation in the range 0.5 - 5%.

Iodine was analyzed in benzene by spectrophotometric measurement at a wavelength of 500 nm ($\varepsilon = 1000\ M^{-1}\ cm^{-1}$) using a 50 mm optical cell. The detection limit was 0.5 µM with a standard deviation in the range 2 - 8%.

Results and discussion

Adsorption of iodate

Adsorption data plotted in Langmuir equation (Figure 2) exhibit a linear segment over the range of concentrations examined at pH 5.7. This observation indicates that only one type of binding site exists for iodate adsorption for our experimental conditions. The Langmuir isotherm gives a concentration of sites equal to 12.7 µmol/g and an equilibrium constant of 1.73×10^{-2} L^2/g^2 at pH 5.7 for an ionic strength of 1 mM. The adsorption of IO_3^- decreases with increasing pH, in agreement with both surface complexation and ligand exchange mechanisms (Figure 2b). At neutral pH, almost no iodate adsorption occurs on synthetic birnessite, which can be explained by the low pH_{zpc} of birnessite (pH_{zpc} = 2.25). At pH 5.0, speciation calculation showed that protonated $\equiv MnOH_2^+$ species would only be present at nanomolar concentrations for a 10 mM δ-MnO_2 suspension (0.87 g/L). Figure 2b shows also that ionic strength has a very low influence on iodate adsorption, which would suggest that adsorption occurs through an inner sphere mechanism.

Determination of rate constants for the oxidation of iodide to iodine

The rate constants for the oxidation of iodide were determined between pH 5.35 and 7.50 in presence of benzene used as extracting solvent of iodine. Both iodide (Figure 3a) and iodine (Figure 3b) were followed in the aqueous and in the organic phases, respectively. The pH values increased immediately after the addition of iodide and remained stable at ±0.15, which allowed the determination of the corresponding rate constants. The results verified that one mole of iodine is formed for two moles of iodide oxidized. Significant iodate formation and thus iodine oxidation was only observed for pH values 5.35 and 6.32 and for reaction times ≥ 3 hours, which explained the discrepancies between experimental and calculated values for iodine in Figure 3b.

The mass balance (i.e. $[I^-]_{ini} = [I^-]_{water} + [IO_3^-]_{water} + 2\ [I_2]_{benz}$) was always verified at 98±4% (n = 37).

The iodide oxidation and the formation of iodine were well modelled assuming a second order reaction with respect to iodide (eq. 2). A reaction second order in iodide was verified by plotting 1/[Iodide] as a function of the reaction time with the slope = $2.k'_{obs}$ (Figure 4). Considering that the concentration of δ-MnO_2 was constant and assuming a first order reaction with respect to δ-MnO_2, the rate constants k_{obs} in $L^2\ mol^{-2}\ s^{-1}$ were then calculated and are given in Table 2 (the value for pH 5.35 was not considered because more than 95% of iodide was oxidized within the first minutes). A second order dependence on iodide was also reported by Laurence and Ellis (1972) for the oxidation of iodide by Fe(III) at acidic pH. Lin et al. (2008) determined a lower order of 1.68 on iodide and a first order on PbO_2 for the reductive dissolution of PbO_2 by iodide.

$$MnO_2 + 2I^- + 4H^+ \longrightarrow Mn^{2+} + I_2 + 2H_2O \qquad k \qquad (2)$$

$$\text{with } -d[I^-]/dt = k'_{obs}\,[I^-]^2 = k_{obs}\,[I^-]^2\,[MnO_2] = k\,[H^+]^n\,[I^-]^2\,[MnO_2]$$

Values of log k_{obs} are plotted as a function of pH in Figure 5. The apparent reaction order with respect to H^+ was determined as the slope of the straight line log k_{obs} = f(pH) and is equal to 2.3. A lower dependence of 0.66 on pH was determined by Lin et al. (2008) between pH 6.0 and 8.0 for the couple PbO_2/I^-. The rate constant k for reaction (2) was found to be $7.2 \times 10^{17}\ M^{-4.3}\ s^{-1}$.

Oxidation of iodide and iodine to iodate

Figure 6 shows data for the oxidation of iodide for varying concentrations of δ-MnO_2 (1 mM to 100 mM) at an initial pH of 5.0 ((a) iodide, (b) reactive iodine species, (c) iodate, (d) pH, (e) mass balance on iodine species). In absence of benzene, reactive iodine species are further oxidized to iodate, which is the end product of iodide oxidation. Even though 3 moles of δ-MnO_2

are reduced per mole of iodide oxidised (eq. 3), under our experimental conditions MnO_2 was always in excess of iodide.

$$I^- + 3MnO_2 + 6H^+ \longrightarrow IO_3^- + 3Mn^{2+} + 3H_2O \qquad (3)$$

For all conditions, the pH increases after the addition of iodide (Figure 6d), which is consistent with the overall reaction of iodide on δ-MnO_2 where the oxidation of one mole of iodide consumes 6 moles of proton. The increase of pH is lower for high concentrations of manganese oxide because of the buffer capacity of manganese oxides:

$$\equiv MnOH + OH^- \rightleftharpoons \equiv MnO^- + H_2O \qquad (4)$$

For high δ-MnO_2 concentrations of 50 mM and 100 mM, the pH remains below 6 and iodide is immediately oxidized to iodate and no iodine is detected. The resulting iodate concentrations (Figure 6c) are 58 µM and 78 µM for 100 mM and 50 mM δ-MnO_2, respectively. The iodate yield is not 100% because of the adsorption of iodate on δ-MnO_2.

It could be expected that iodate adsorption could decrease the rate of iodide oxidation by competitive adsorption at the reactive sites. Experiments with initial iodide concentration of 50 µM and 10 mM δ-MnO_2 carried out at an initial pH of 5 in absence and in presence of 50 µM iodate showed no effect of iodate on the oxidation rate of iodide (results not shown).

For δ-MnO_2 concentrations of 5 mM and 10 mM, pH values increase to 6.5 (Figure 6e). This reduces the oxidation rate of iodide. Reactive iodine species are formed within the first 30 minutes and slowly decayed by formation of iodate. The oxidation of iodide to iodine is then faster than the oxidation of iodine to iodate in agreement with the calculation of the driving forces between pH 4 to 8 (Figure 1).

Reactive iodine species are only detected when $[I^-] > 10$ µM (Figure 6a and 6b), which can be related to the formation of elemental iodine according to the equilibrium:

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \qquad K = 5.44 \times 10^{-13} \text{ Burger and Liebhafsky (1973)} \quad (5)$$

According to the above equilibrium, iodine represents ≥ 85% of the reactive iodine species at pH 6.5, and for [I^-] ≥ 10 µM. The presence of I_2 was confirmed by the UV/visible spectra of the filtered solution that exhibited a peak maximum at 460 nm. The formation of triiodide is unlikely in our conditions i.e. for µmolar concentrations of iodide:

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K = 725 \qquad \text{Burger and Liebhafsky (1973)} \quad (6)$$

The mass balance of iodine (Figure 6e), calculated by considering that all reactive iodine species are molecular iodine, shows that for the highest concentrations of iodine (i.e. I_2 = 15 µM for 5 mM δ-MnO_2 and I_2 = 20 µM for 10 mM δ-MnO_2 at 30-minutes reaction time) there is a deficit of 20 to 25 µM. The deficit cannot be explained by iodate adsorption because iodate adsorption is low at pH 6 and it is observed at the beginning of the reaction i.e. for low iodate concentration (e.g. 6 µM for 5 mM δ-MnO_2 and 30-min reaction time).

The oxidation of iodine to iodate was studied for an initial concentration of iodine of 48 µM and 10 mM δ-MnO_2 at an initial pH of 5.0 (Figure 7). During the first minute of the reaction, 13.6 µM of iodine disappeared immediately from the solution and 9.7 µM of iodate were formed. Thus, about 9 µM of iodine would be adsorbed on manganese oxides, which would explain the deficit in iodine observed in the previous experiments. The loss of iodine is accompanied by an increase of the pH from 5.0 to 5.9 within the first minute. After that initial pH change it remains constant throughout the experiment. This observation would be consistent with a ligand exchange mechanism between iodine and hydroxide ions. For the next three hours iodine is further oxidised to iodate with a stoichiometric factor of 2 (I_2:IO_3^- = 1:2). Sites on manganese oxide can then be considered as Lewis acid sites i.e. sites capable of receiving an electron pair from the adsorbate. Similarly, an inner-sphere mechanism was also proposed for the oxidation of sulfite on manganese dioxide (Herszage and Dos Santos Afonso, 2003). The complexation of iodine by MnO_2 would result in the polarisation of the I-I bond i.e. the electron density of manganese increases whereas the electron density of iodine decreases. This would enhance the reactivity of iodine towards electrophilic substitution and thus the formation of iodinated organic compounds. Such activation of the iodine molecule by mineral oxide catalysts is commonly used in organic synthesis (Stavber et al., 2008).

The reduction of metal oxides by iodide involves several reaction steps including adsorption of iodine on the metal oxide surfaces, electron transfer between iodine and the metal oxide and release of the oxidized species and the reduced metal ions:

$$MnO_2 + I_2 \rightleftharpoons (MnO_2 - I_2) \qquad K \qquad (7)$$

$$(MnO_2 - I_2) \longrightarrow 2\,IO_3^- + Mn^{II} \qquad k_c \qquad (8)$$

Such reaction mechanisms can be described by a Langmuir-Hinshelwood or Michaelis–Menten type rate law where the apparent reaction order vary between 0 and 1 depending on the rate limiting step. When adsorption is the rate limiting step, the reaction is first order with respect to the concentration of I^- or I_2 and first order with respect to the metal oxide concentration (MnO_2). When electron transfer is the rate limiting step, the rate is proportional to the concentration of surface complexes (MnO_2-I_2). When the concentration of the reductive species reaches a concentration where all the reactive sites are saturated, the concentration of the surface complex is constant and the reaction rate is zero order. Before saturation, the rate is also first order with respect to the reductive species and the metal oxide surface. The second order rate constant k_{app} of iodine oxidation is the product of the equilibrium constant K and the rate constant of the decomposition of the surface complex k_c (eq. 9).

$$- d[I_2]/dt = k_c\,[MnO_2 - I_2] = k_c\,K\,[MnO_2]\,[I_2] = k_{app}\,[MnO_2]\,[I_2] \qquad (9)$$

Because $[MnO_2]$ was in excess compared to $[I_2]$, the plot of $\ln[I_2]/[I_2]_o$ versus reaction time after the initial adsorption phase gave a straight line with an apparent first order rate constant $k'_{app} = 2.57 \times 10^{-4}\ s^{-1}$ ($r^2 = 0.993$, n = 14). By taking into account both iodine concentration in solution and the I_2 concentration adsorbed on MnO_2 (i.e. $[MnO_2 - I_2]$), a rate constant $k_c = 1.0 \times 10^{-3}\ s^{-1}$ was then calculated for the decomposition of the surface complex (eq. 10).

$$- d[I_2]/dt = k'_{app}[I_2] = k_c [MnO_2 - I_2] \ , \ k_c = \frac{k'_{app}.[I_2]}{[MnO_2 - I_2]} \qquad (10)$$

Effect of pH

Figure 8 shows the effect of pH on the kinetics of the oxidation of iodide and the formation of iodate and active iodine species. As expected from the driving force (ΔpE) (see Figure 1) and from previous experiments conducted in presence of benzene, the rates of iodide oxidation (Figure 8a) and iodate formation (Figure 8b) strongly increase with decreasing pH. Reactive iodine species are formed within the first 30 minutes except for pH 7 where a slower formation was observed (Figure 8c). For an initial $pH \leq 6$, the formation of iodine on δ-MnO_2 is accompanied by an increase in pH for the first 30 minutes of the reaction (Figure 8d). At an initial pH of 8, about 6 µM of iodide disappear immediately after δ-MnO_2 addition probably by simple sorption onto the manganese dioxide surface. Nevertheless, slow oxidation of iodide also occurs at pH 7.3-7.4 (initial pH 8). An iodate formation rate of 0.7 µM/h was determined. For this condition, iodine could not be detected in solution. Iodine was quantified for all the other pH conditions (Figure 8c). Results showed that the iodine exposure i.e. the integral of the iodine concentration versus time curve is higher in the pH range 6 – 7 than at readily acidic pH because at pH < 6 iodide is rapidly converted to iodate.

Effect of ionic strength

The effect of ionic strength on iodide oxidation and iodine and iodate formation was studied for ionic strength from 0.1 to 10 mM $NaClO_4$. Results in Figures 9 show that for an increase in ionic strength, the stability of reactive iodine species in solution increased (Figure 9a) and thus the rate of iodate formation decreased (Figure 9b). The apparent first order rate constants of oxidation of iodine determined from data plotted in Figure 9a linearly decreased with $I^{1/2}$ (Figure 10). The mass balance for iodine at 30 minutes was 72% for 1 mM $NaClO_4$, 64% for 5 mM and 57% for 10 mM. Because iodate adsorption is negligible at pH 6.2 – 6.5, this suggests that the adsorption of reactive iodine species increases when the ionic strength increases.

One possible explanation of the negative effect of ionic strength on the oxidation of reactive iodine species could be the change of speciation between I_2 and HOI. When ionic strength increases, the hydrolysis of iodine (reaction 7) is shifted to HOI, which is expected to be more stable than I_2 in presence of manganese oxide. However, the ionic strength corrections using the Debye-Hückel equation shows that the HOI/I_2 ratio only increases from 0.174 to 0.193 for 0.1 mM to 10 mM ionic strength (calculations were done for pH = 6.5 and $[I^-]$ = 10 µM). Thus, the speciation of HOI/I_2 cannot only account for the effect of ionic strength observed in our conditions.

Ionic strength can also directly affect the reactivity of manganese dioxide. In aqueous solution, freshly prepared δ–MnO_2 particles are aggregates of size ranging from about 0.2 and 0.4 µm. The size grows to 1.0 µm over period of months, which was explained by coagulation (Stone and Morgan, 1984). Thus, the coalescence of particles was proposed to be partly responsible of the decrease of reactivity (e.g. rates of reduction by phenolic compounds) observed during aging of manganese oxides (Stone and Morgan, 1984). In our experiments, increasing ionic strength also increases the size of MnO_2 aggregates by coagulation, which might explain the decrease of the rate of iodate formation. Increasing ionic strength decreases also the water solubility and favors hydrophobic interactions. Thus, and because of the strong hydrophobicity of iodine, the increase of iodine adsorption with increasing ionic strength might be due to hydrophobic interactions between iodine and manganese oxide particles. Hydrophobic interactions have already been proposed to explain the adsorption of certain organic compounds on MnO_2 (Bernard et al., 1997). The hydrophobic interactions are long range interactions, which might also cause a reduction of the rate of electron transfer between iodine and the MnO_2 surface when ionic strength increases.

Implications for water treatment

Our results show that iodine can be produced at near neutral pH when iodide containing waters are in contact with manganese oxide. In water treatment, manganese oxides are commonly used for Mn removal. Even though the residence times in MnO_2 filters are only 10 - 15 minutes and iodide concentrations are usually in the ppb range, the formation of low amount of iodine might result in the formation of iodinated organic compounds. Our results give also evidence that iodine readily adsorbs on synthetic birnessite. In absence of organic compounds, the complexation of iodine is followed by electron transfer with formation of iodate. Iodate is the desired sink for water utilities, because it is inert and non-toxic (Burgi et al., 2001). The results suggest that the formation of iodinated organic compounds can be reduced by 1) maintaining high pH values > 7.5 to limit iodine formation or 2) by lowering the pH around 5.0 to rapidly convert iodide to stable iodate. Mineral content of natural waters would also influence the formation of iodinated organic compounds because reactive iodine species have been found more stable when ionic strength increases from 0.1 mM to 10 mM. The presence of specific mineral species such as carbonate and sulfate might also affect the formation of iodinated organic compounds by competing with iodine for adsorption/activation on manganese dioxide.

Conclusion

The oxidation of iodide to iodate by synthetic birnessite was studied between pH 4 and 8 for different conditions.

- Iodate slightly adsorbs on birnessite at pH 5.7 with adsorption capacity of 12.7 µmol/g. The adsorption decreases with increasing pH. At circumneutral pH the adsorption is not significant.
- The rate of iodide oxidation decreases with increasing pH with an H^+ dependence of 2.3. Third order rate constants, second order in iodide and first order in δ-MnO_2, were determined and varied from 1790 M^{-2} s^{-1} at pH 6.30 to 3.1 M^{-2} s^{-1} at pH 7.50.
- Iodine was detected as a reactive intermediate species in the oxidation of iodide to iodate, especially for the lowest MnO_2/I^- ratios and for a pH range between 6.0 and 7.0. For a high MnO_2/I^- ratio and pH < 6, iodide is rapidly converted to iodate and therefore iodine was not observed.
- Increasing the ionic strength from 10^{-4} to 10^{-2} M reduces the rate of iodate formation by decreasing the oxidation rate of iodine. Therefore the iodine exposure is higher for high ionic strengths.
- Iodine significantly adsorbs on synthetic birnessite that reacts as a Lewis acid by receiving an electron pair. Complexation of iodine on manganese oxides might contribute to the activation of iodine through to the polarization of the I – I bond. Complexed or free iodine can then react with natural organic matter in the environment and in water treatment processes to produce iodinated organic compounds in the pH range 6.0 – 7.0.
- Further research is needed to evaluate the potential formation of iodinated organic compounds like iodo-THMs (iodoform) when iodide-containing natural waters are treated by manganese oxides.

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Table 1. Half reactions, $E_H°$ and $p\varepsilon°$ (log K) for Mn and iodine species. The $E_H°$ and $p\varepsilon°$ (log K) is for the standard state condition (1M in all species including H^+).

Table 2. Third order rate constants k_{obs} in L^2 mol^{-2} s^{-1} for the oxidation of iodide by δ-MnO_2 (25°C, 1 mM $NaClO_4$)

Table 1.

Half reactions	$E_H°$ in V	$p\varepsilon°$ (log K)
$\frac{1}{2} MnO_2 + 2 H^+ + e^- \rightleftharpoons \frac{1}{2} Mn^{2+} + H_2O$	1.29	21.86
$\frac{1}{2} I_{2(aq)} + e^- \rightleftharpoons I^-$	0.615	10.42
$1/5\ IO_3^- + 6/5\ H^+ + e^- \rightleftharpoons 3/5\ H_2O + 1/10\ I_{2(aq)}$	1.178	19.96
$1/6\ IO_3^- + H^+ + e^- \rightleftharpoons \frac{1}{2} H_2O + 1/6\ I^-$	1.085	18.38

Table 2.

pH	k_{obs}
6.32	1790 ±280
6.73	250 ±14
6.80	72 ±3
7.39	5.5 ±0.8
7.50	3.1 ±0.2

Figure 1. Δlog K vs. pH plots for redox reactions between iodine species and δ-MnO_2. Calculations were made using pε° in Table 1 and for $\{I_2\} = \{IO_3^-\} = \{I^-\} = 1$. Low activity of Mn^{2+} of 10^{-7} was used for calculation because Mn^{2+} was considered to be catalytically reoxidized by oxygen in presence of MnO_2. Negative log K values indicate unfavourable reactions.

Figure 2. Adsorption of iodate on δ-MnO_2 (a) adsorption isotherm ([δ-MnO_2] = 10 mM, $NaClO_4$ 1 mM, pH 5.7) (b) effect of pH and ionic strength ([δ-MnO_2] = 10 mM; $[IO_3^-]_o$ = 100 µM)

Figure 3. Kinetics of (a) iodide oxidation and (b) iodine formation (experimental data (symbols) and third order kinetic model (line); [δ-MnO_2] = 10 mM, $[I^-]_o$ = 100 µM, I = 1 mM $NaClO_4$, the pH values are constant pH values ±0.15 for reaction times > 30 min.).

Figure 4. Plot of $1/[I^-]$ versus time for iodide oxidation by δ–MnO_2 ([δ-MnO_2] = 10 mM, $[I^-]_o$ = 100 µM, I = 1 mM $NaClO_4$)

Figure 5. Dependence of the third order rate constant k_{obs} on pH (I = 1 mM $NaClO_4$)

Figure 6. Evolution of iodine species and pH for varying concentrations of δ-MnO_2 ($NaClO_4$ 1 mM, initial pH 5, $[I^-]$ = 100 µM). (a) iodide, (b) reactive iodine species (i.e. I_2 + HOI), (c) iodate, (d) pH, (e) mass balance for iodine species.

Figure 7. Reaction of δ-MnO_2 with iodine (I_2) (δ-MnO_2] = 10 mM, $[I_2]_o$ = 48 µM, $NaClO_4$ 1 mM)

Figure 8. Effect of pH on the kinetics of the oxidation of iodide (a), the formation of iodate (b) and reactive iodine species (c), (d) shows the evolution of the pH ([δ-MnO_2] = 10 mM, $[I^-]_o$ = 100 µM, $NaClO_4$ 1mM).

Figure 9. Effect of ionic strength on iodate and iodine formation ([δ-MnO_2] = 10 mM, $[I^-]_o$ = 100 µM, initial pH 5.0, final pH 6.2-6.5)

Figure 10. Effect of ionic strength on the apparent first order rate constant of iodine oxidation ([δ-MnO_2] = 10 mM, $[I^-]_o$ = 100 µM, pH 6.2 – 6.5)

Figure 1.

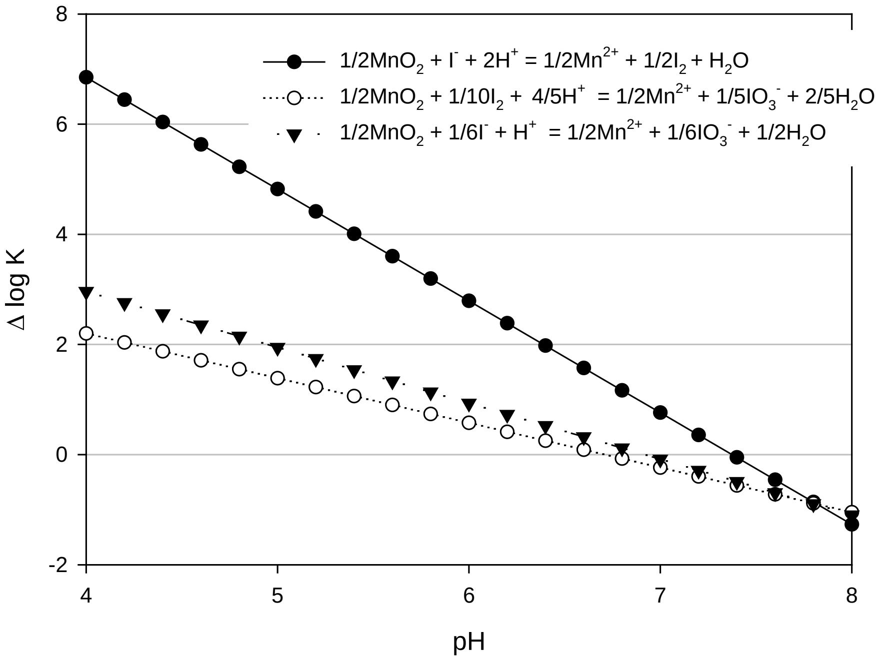

8
6
4
2
0
-2
Δ log K
4
5
6
7
8
pH
$1/2MnO_2 + I^- + 2H^+ = 1/2Mn^{2+} + 1/2I_2 + H_2O$
$1/2MnO_2 + 1/10I_2 + 4/5H^+ = 1/2Mn^{2+} + 1/5IO_3^- + 2/5H_2O$
$1/2MnO_2 + 1/6I^- + H^+ = 1/2Mn^{2+} + 1/6IO_3^- + 1/2H_2O$

Figure 2.

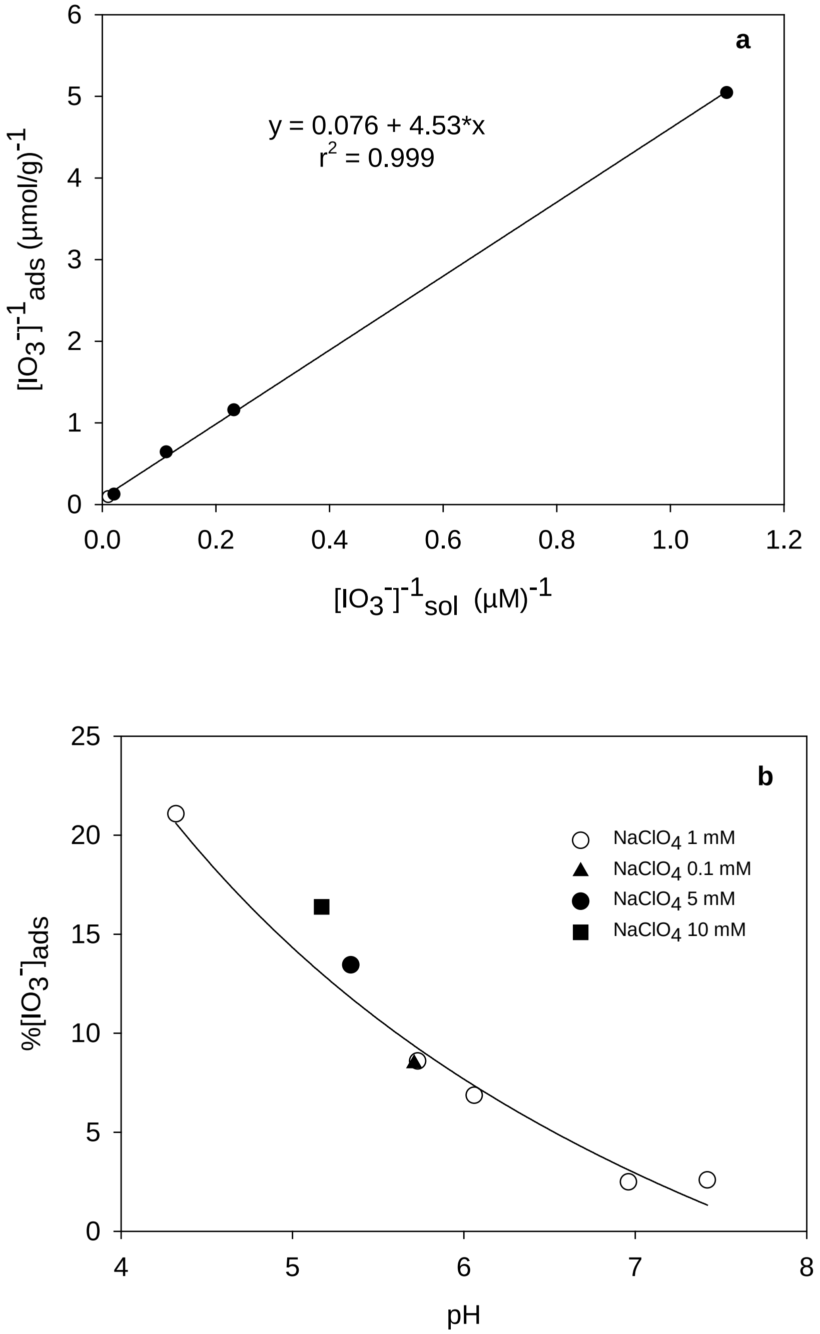

a
y = 0.076 + 4.53*x
r2 = 0.999
[IO3-]-1ads (µmol/g)-1
[IO3-]-1sol (µM)-1
0
1
2
3
4
5
6
0.0
0.2
0.4
0.6
0.8
1.0
1.2
b
NaClO4 1 mM
NaClO4 0.1 mM
NaClO4 5 mM
NaClO4 10 mM
%[IO3-]ads
pH
0
5
10
15
20
25
4
5
6
7
8

Figure 3.

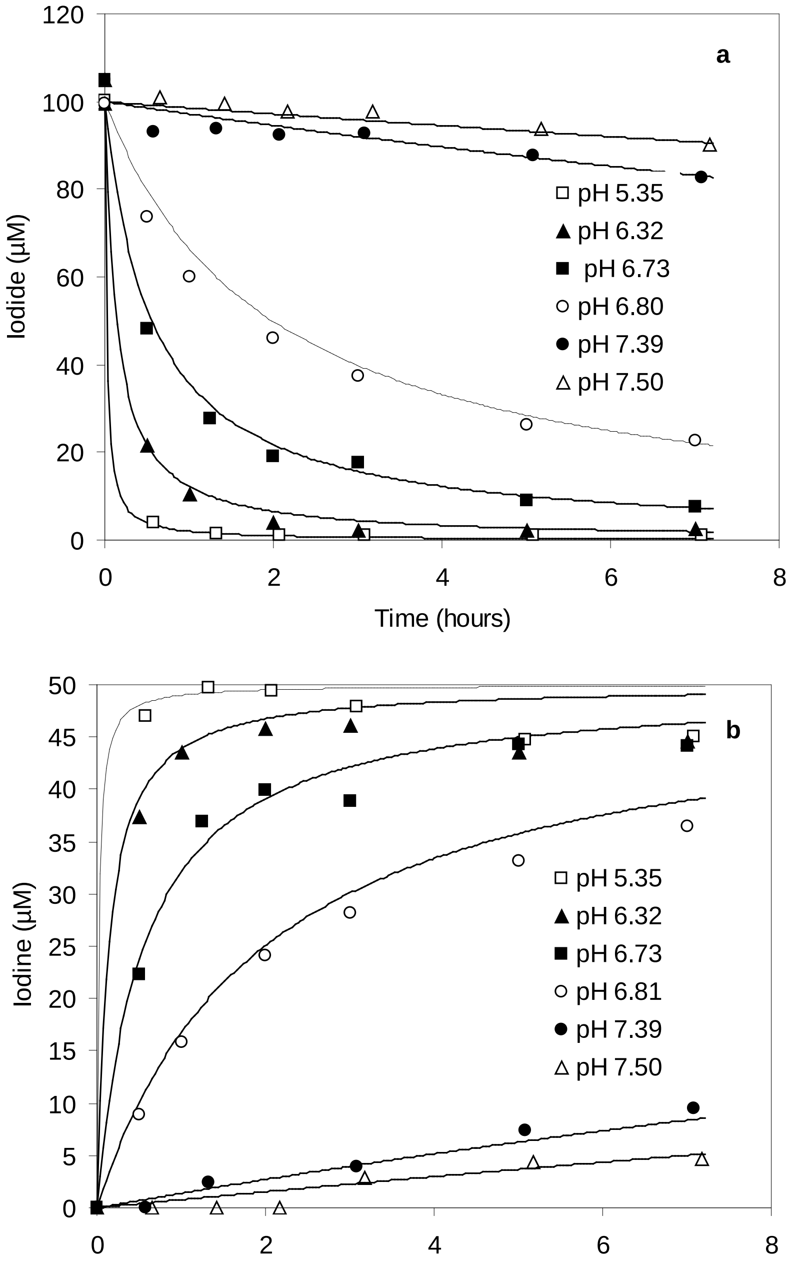

a
Iodide (µM)
120
100
80
60
40
20
0
Time (hours)
0
2
4
6
8
□ pH 5.35
▲ pH 6.32
■ pH 6.73
○ pH 6.80
● pH 7.39
△ pH 7.50
b
Iodine (µM)
50
45
40
35
30
25
20
15
10
5
0
Time (hours)
0
2
4
6
8
□ pH 5.35
▲ pH 6.32
■ pH 6.73
○ pH 6.81
● pH 7.39
△ pH 7.50

Figure 4.

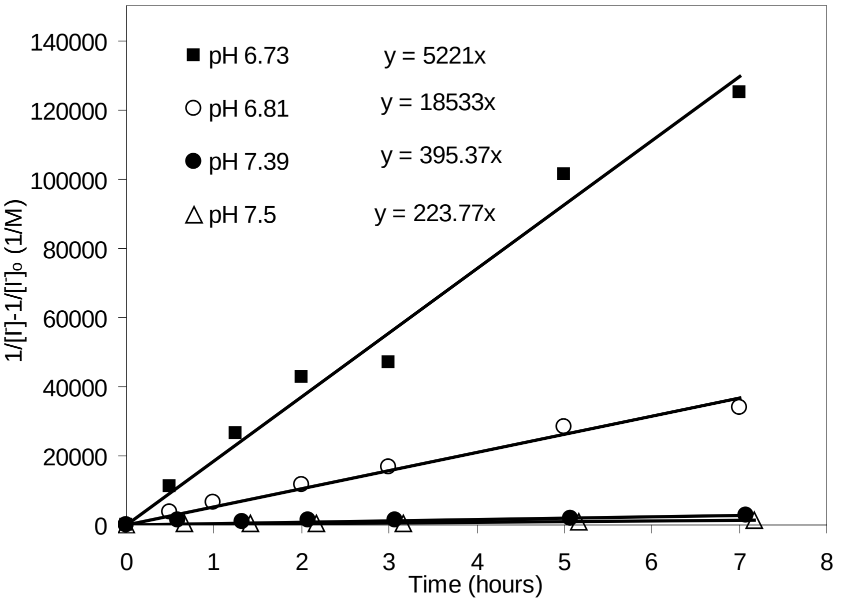

■ pH 6.73
○ pH 6.81
● pH 7.39
△ pH 7.5
y = 5221x
y = 18533x
y = 395.37x
y = 223.77x
1/[I⁻]-1/[I⁻]₀ (1/M)
140000
120000
100000
80000
60000
40000
20000
0
0
1
2
3
4
5
6
7
8
Time (hours)

Figure 5.

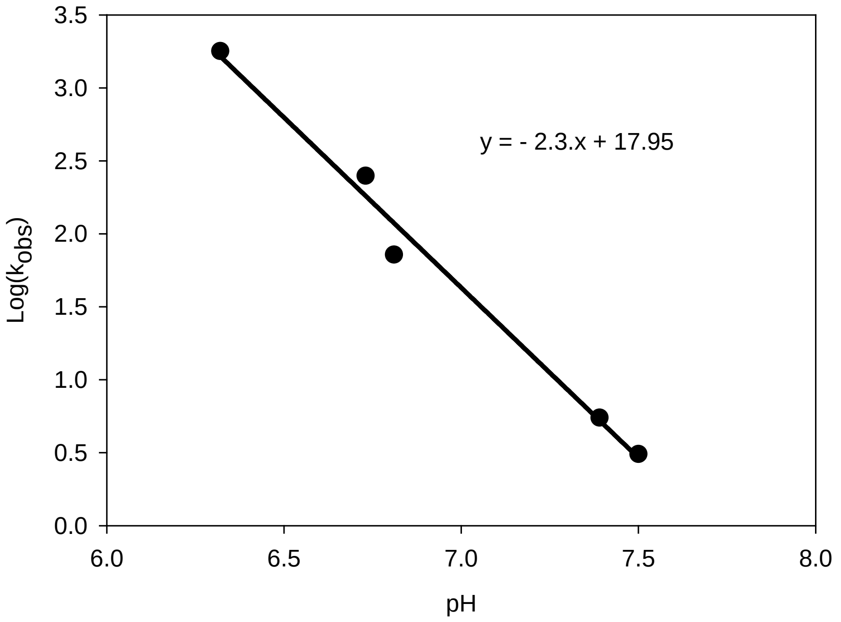


Figure 6.

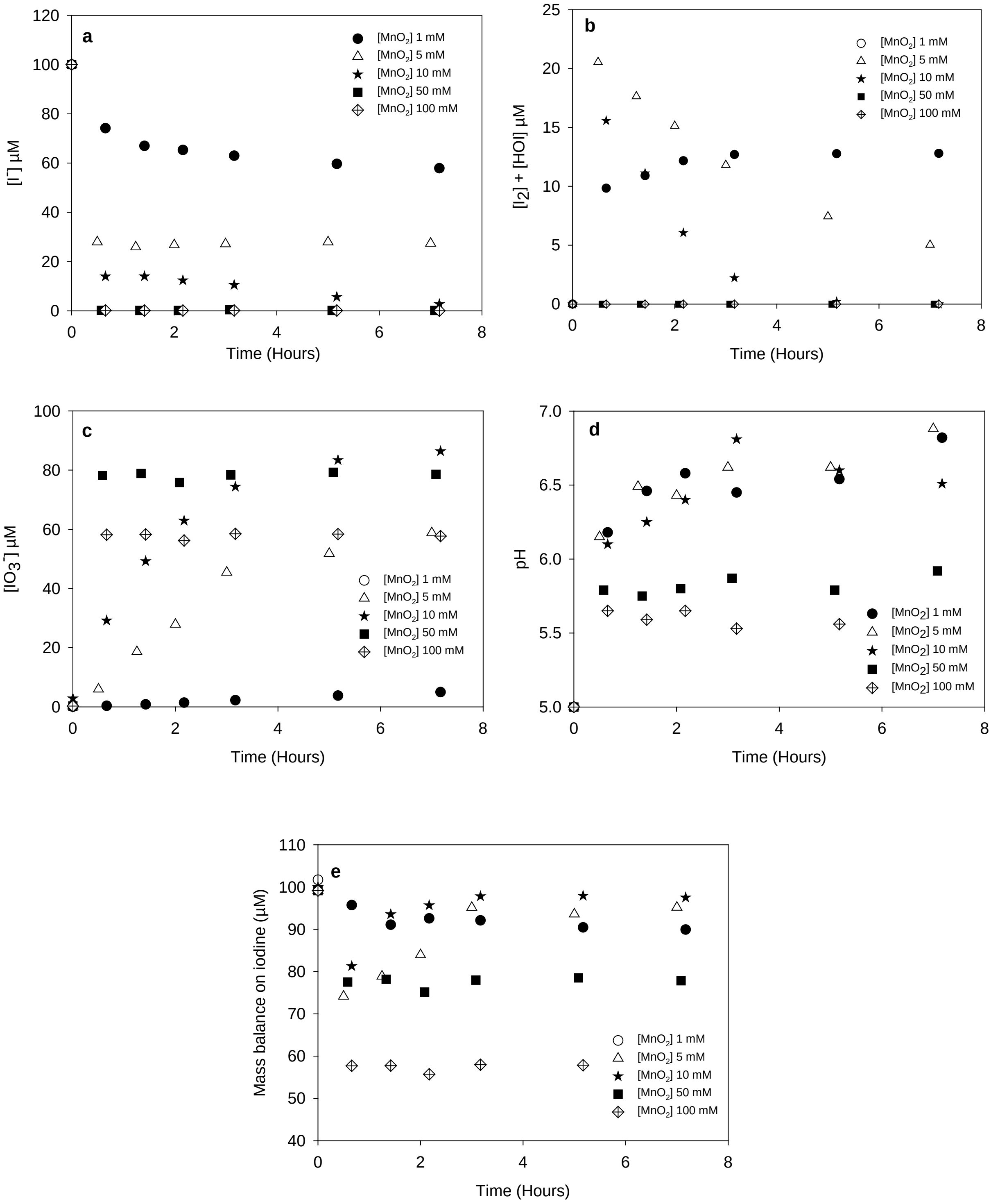

a
[I⁻] µM
0
20
40
60
80
100
120
Time (Hours)
0
2
4
6
8
[MnO2] 1 mM
[MnO2] 5 mM
[MnO2] 10 mM
[MnO2] 50 mM
[MnO2] 100 mM
b
[I2] + [HOI] µM
0
5
10
15
20
25
Time (Hours)
0
2
4
6
8
[MnO2] 1 mM
[MnO2] 5 mM
[MnO2] 10 mM
[MnO2] 50 mM
[MnO2] 100 mM
c
[IO3⁻] µM
0
20
40
60
80
100
Time (Hours)
0
2
4
6
8
[MnO2] 1 mM
[MnO2] 5 mM
[MnO2] 10 mM
[MnO2] 50 mM
[MnO2] 100 mM
d
pH
5.0
5.5
6.0
6.5
7.0
Time (Hours)
0
2
4
6
8
[MnO2] 1 mM
[MnO2] 5 mM
[MnO2] 10 mM
[MnO2] 50 mM
[MnO2] 100 mM
e
Mass balance on iodine (µM)
40
50
60
70
80
90
100
110
Time (Hours)
0
2
4
6
8
[MnO2] 1 mM
[MnO2] 5 mM
[MnO2] 10 mM
[MnO2] 50 mM
[MnO2] 100 mM

Figure 7

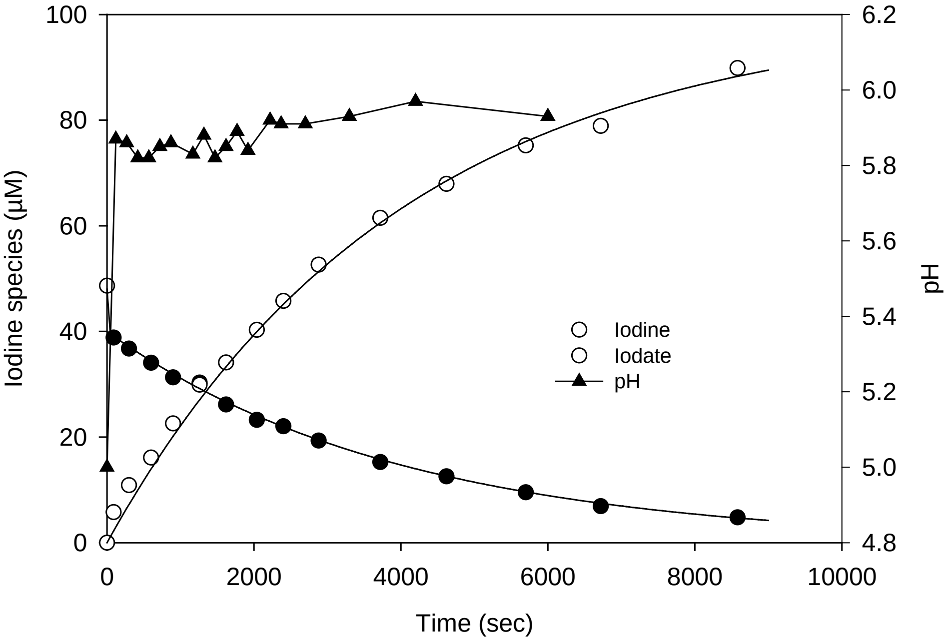

Iodine species (µM)
0
20
40
60
80
100
pH
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
Time (sec)
0
2000
4000
6000
8000
10000
Iodine
Iodate
pH

Figure 8.

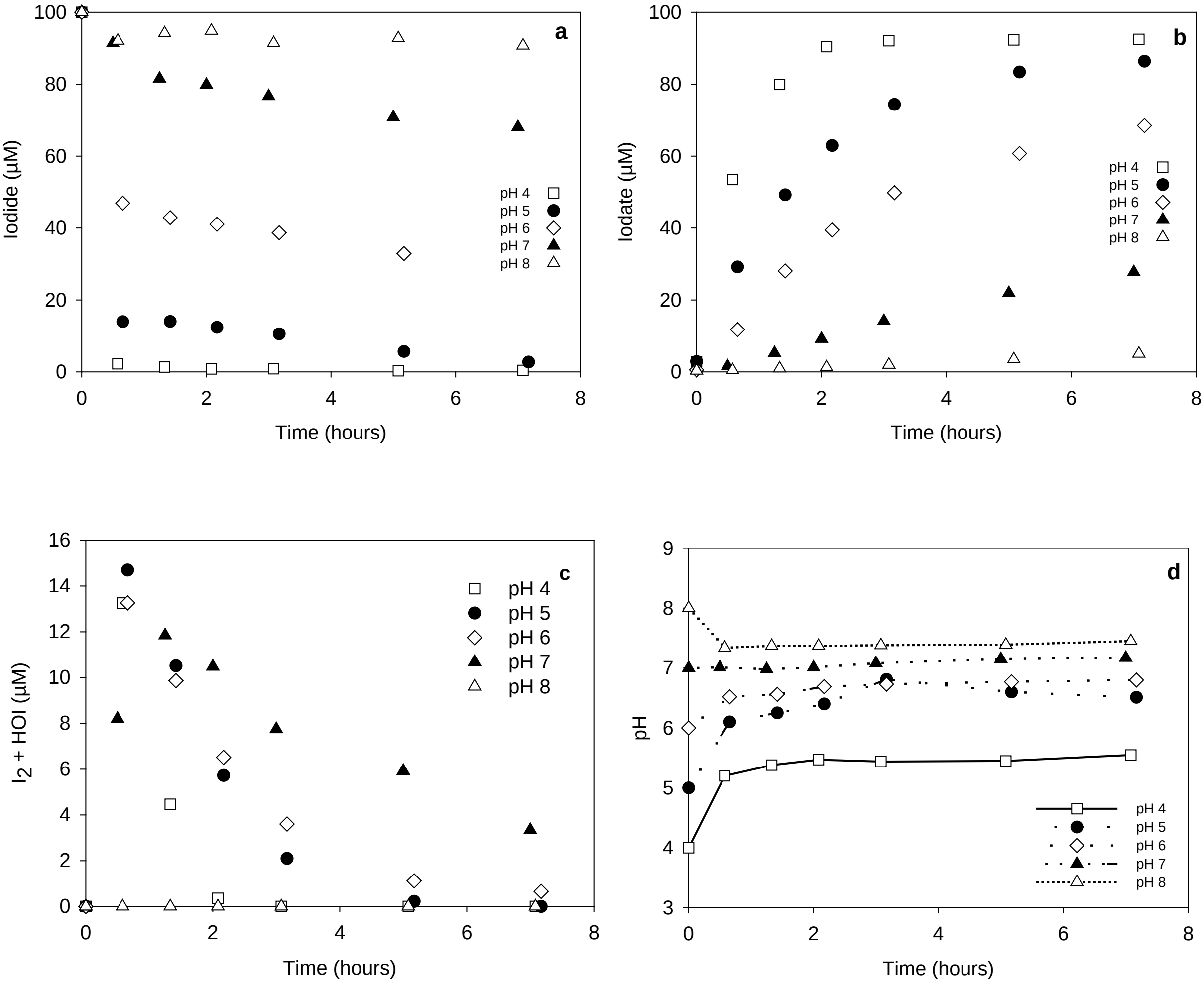

a
Iodide (µM)
Time (hours)
0
20
40
60
80
100
0
2
4
6
8
pH 4 □
pH 5 ●
pH 6 ◇
pH 7 ▲
pH 8 △
b
Iodate (µM)
Time (hours)
pH 4 □
pH 5 ●
pH 6 ◇
pH 7 ▲
pH 8 △
c
I_2 + HOI (µM)
Time (hours)
0
2
4
6
8
10
12
14
16
pH 4 □
pH 5 ●
pH 6 ◇
pH 7 ▲
pH 8 △
d
pH
Time (hours)
3
4
5
6
7
8
9
pH 4
pH 5
pH 6
pH 7
pH 8

Figure 9

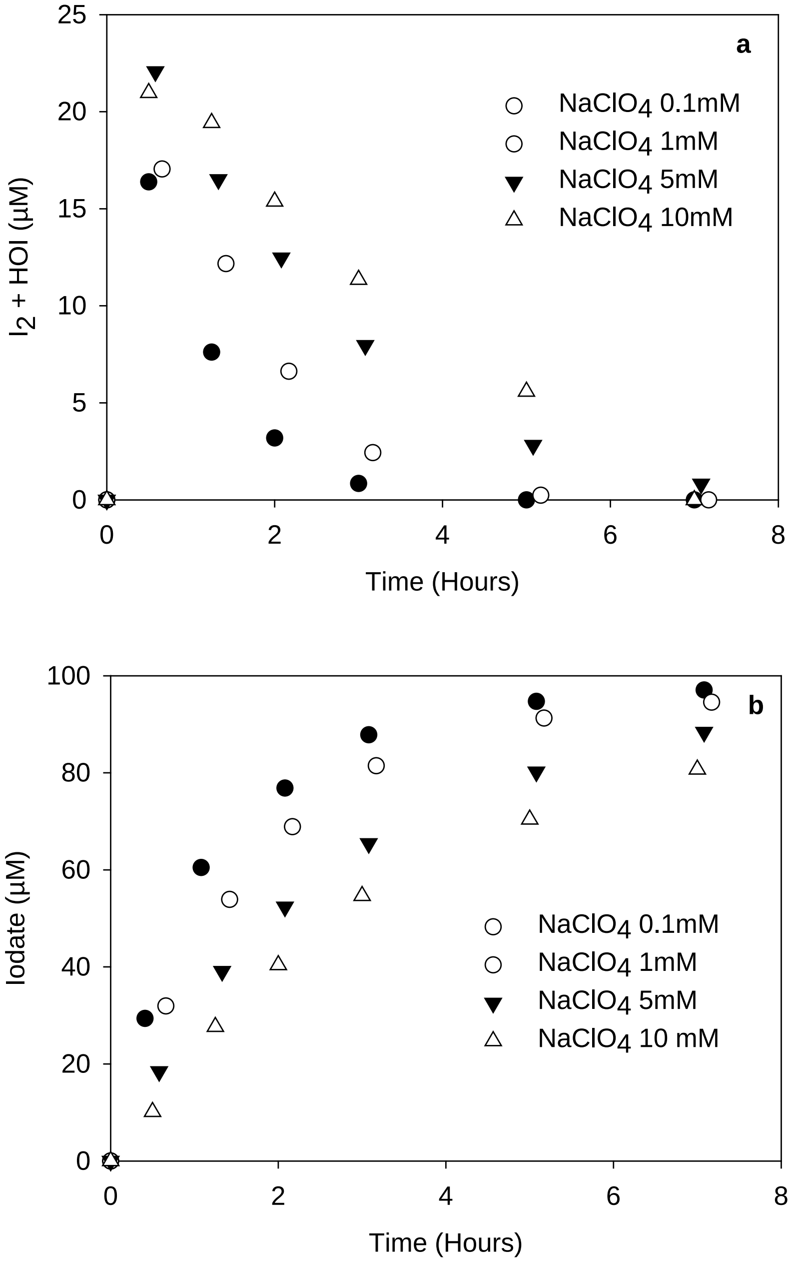
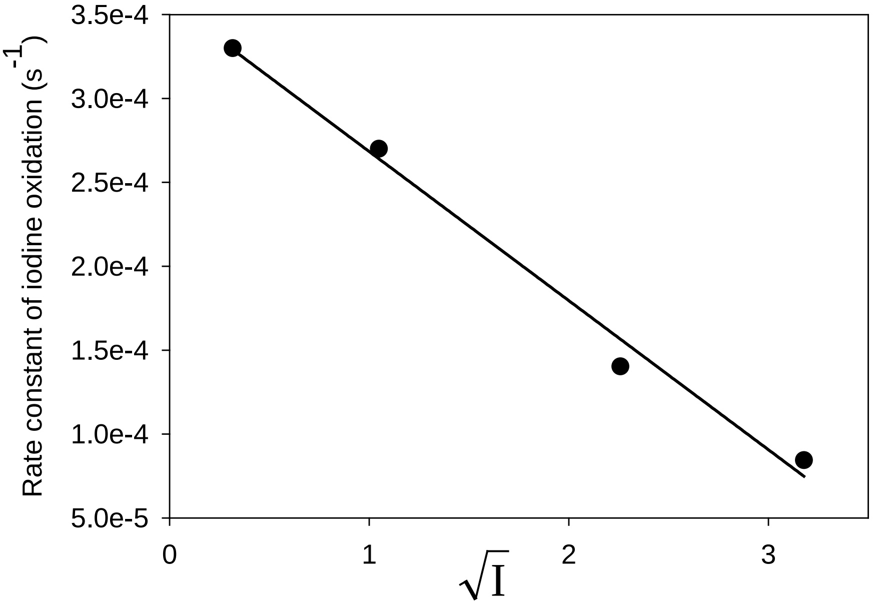

a
NaClO4 0.1mM
NaClO4 1mM
NaClO4 5mM
NaClO4 10mM
I2 + HOI (µM)
0
5
10
15
20
25
Time (Hours)
0
2
4
6
8
b
NaClO4 0.1mM
NaClO4 1mM
NaClO4 5mM
NaClO4 10 mM
Iodate (µM)
0
20
40
60
80
100
Time (Hours)
0
2
4
6
8

Figure 10.


Rate constant of iodine oxidation (s^{-1})
3.5e-4
3.0e-4
2.5e-4
2.0e-4
1.5e-4
1.0e-4
5.0e-5
0
1
2
3
$\sqrt{I}$