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Aerobic and anaerobic oxidation of ferrous ions in near-neutral solutions

Shishir Mundra^{a,*}, Jan Tits^b, Erich Wieland^b, Ueli M. Angst^a

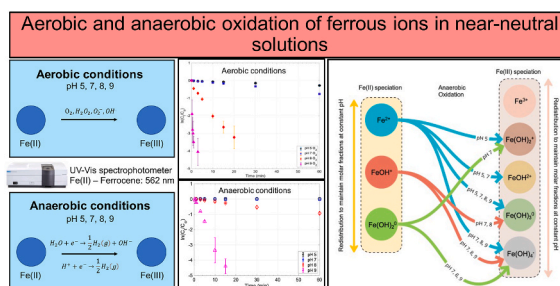
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HIGHLIGHTS

- Oxidation of Fe(II) in aerobic and anaerobic conditions is investigated.
- Fe(II) oxidation in anaerobic conditions is first order w.r.t. [Fe(II)].
- Oxidation proceeds with set of parallel reactions involving different hydrolysed and non-hydrolysed Fe(II) and Fe(III) species.
- In the absence of oxygen, the cathodic reaction accompanying oxidation of Fe(II), is the reduction of H₂O releasing H₂ (g).
- An increase in the pH leads to increase Fe(II) oxidation rates.
- Speciation of Fe(II) and Fe(III), the presence of other anions and the pH of the solution are critical parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

Whilst the oxidation of Fe(II) in aerobic conditions has been studied thoroughly, an in-depth knowhow on the fate or stability of Fe(II) in solutions with near-neutral pH under anaerobic conditions is still lacking. Here, we experimentally investigated the kinetics of Fe(II) oxidation in solutions with pH ranging between ~5 and 9, under aerobic (when solutions were in equilibrium with atmospheric oxygen) and anaerobic conditions (when the dissolved oxygen concentration was $\sim 10^{-10}$ mol/L), by colorimetric means. Experimental results and thermodynamic considerations presented here, show that Fe(II) oxidation in anaerobic conditions is first-order w.r.t. [Fe(II)], and proceeds with set of parallel reactions involving different hydrolysed and non-hydrolysed Fe(II) and Fe(III) species, similar to that observed in aerobic conditions. However, in the absence of oxygen, the cathodic reaction accompanying the anodic oxidation of Fe(II), is the reduction of H₂O (l) releasing H₂ (g). Hydrolysed Fe(II) species oxidise much faster than Fe²⁺ and their concentrations increases with pH, leading to increased Fe(II) oxidation rates. Additionally, we also show the importance of the type of buffer used to study Fe(II) oxidation. Therefore, for the oxidation of Fe(II) in near-neutral solutions, the speciation of Fe(II) and Fe(III), the presence of other anions and the pH of the solution are critical parameters that must be considered. We anticipate that our results and hypothesis will find use in reactive-transport models simulating different processes occurring in anaerobic conditions such as corrosion of the steel in concrete structures, or in nuclear waste repositories.

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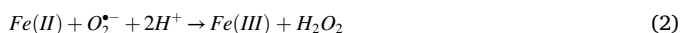
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1. Introduction

Iron, one of the most abundant metals, is an ubiquitous material influencing processes that have long lasting impacts on eco-systems occurring at varied scales (Posner, 1953; Cher and Davidson, 1955; Huffman and Davidson, 1956; Stumm and Lee, 1961; Angst, 2018), from the microbial level to the infrastructural scale. The chemistry of aqueous iron plays a central role in biological and chemical processes, and therefore, has been the subject of extensive work over the last century (Posner, 1953; Cher and Davidson, 1955; Huffman and Davidson, 1956; Stumm and Lee, 1961; Angst, 2018; Millero, 1985; Millero et al., 1987; Weiss, 1935). The majority of the studies in the literature have focussed on the stability, mechanisms and kinetics of oxidation Fe(II) (aq) in the context of ferrous ions being a critical micronutrient for biological uptake by microbial organisms (Pham and Waite, 2008), water pollution in distribution systems and the occurrence of 'red waters' due to internal corrosion of iron pipes (Stumm and Lee, 1961), limnology (Boyle et al., 1977; Sholkovitz, 1976; Murray and Gill, 1978; Emmenegger et al., 1998), oceanography (Byrne and Kester, 1976a, 1976b), wastewater control (Roekens and Van Greiken, 1984; Lowson, 1982), groundwater chemistry and the leaching of minerals (Stumm, 1990). In the case of porous materials and anaerobic environments, such as those encountered in a nuclear waste repository (bentonite clays) (Leupin et al., 2021; Kursten et al., 2021) or steel-reinforced concrete or soils (Stefanoni et al., 2018, 2019), the oxidation of ferrous ions competes with diffusion and precipitation of thermodynamically stable iron oxides, and can have significant influences on the corrosion rate as well as the service-life of the structure.

In aqueous environments, iron can exist as ferrous (Fe(II)) or ferric (Fe(III)) ions or their respective hydrolysed forms depending on the pH. In near-neutral solutions, Fe(II) is more soluble than Fe(III), however, Fe(III) is thermodynamically more stable (Pham and Waite, 2008). Owing to its low solubility in near-neutral environments, Fe(III) hydrolyses and precipitates as insoluble iron hydr(oxides). The kinetics of Fe(II) oxidation is therefore important to completely understand the redox chemistry of iron in near-neutral environments. The oxidation kinetics of Fe(II) (aq) is influenced strongly by the pH of the solution, the temperature, the oxygen concentration and interactions with other ionic species in the solution.

A mechanism for iron oxidation in the presence of oxygen dates back to the 1930's, when Weiss (1935) proposed that intermediate reactive oxygen species such as $O_2^{\bullet-}/HO_2^{\bullet}$, OH^{\bullet} , H_2O_2 were involved in the process. In near-neutral conditions, other anions such as Cl^- or CO_3^{2-}/HCO_3^- have been observed to outcompete Fe(II) for OH^{\bullet} (King et al., 1995), thereby limiting the role of OH^{\bullet} in the oxidation process. Intermediates such as $O_2^{\bullet-}$ and H_2O_2 were found to play a far more important role in the oxidation behaviour of Fe(II) (Pham and Waite, 2008). Recent studies (Pham and Waite, 2008; Santana-Casiano et al., 2004, 2005) concerning the oxidation of Fe(II) at nanomolar concentrations and in the presence of low bicarbonate concentrations, have also shown that the back reduction of Fe(III) with $O_2^{\bullet-}$ should also be taken into account in modelling the overall oxidation kinetics. Considering the importance of all the intermediate species involved in the oxidation process, particularly relevant at circumneutral pH, King et al. (1995) described the oxidation of Fe(II) (similar to Weiss) through the following reactions (Eqs. (1)–(4)), with reactions described by Eq. (1) and/or 3 being rate-limiting:



The overall oxidation kinetics of Fe(II) is generally described as a

function of [Fe(II)], oxygen concentration and the pH of the solution ($5 < \text{pH} < 8$), by the following relationship (Eq. (5)) (Stumm and Lee, 1961; Millero, 1985):

$$\frac{dFe(II)}{dt} = -k[Fe(II)][OH^-]^2[O_2] \quad (5)$$

where, k ($M^{-3}s^{-1}$) is the overall oxidation rate constant. Eq. (5) is often written with the partial pressure of oxygen (pO_2) instead of the dissolved oxygen concentration, assuming that the experimental solution is in equilibrium with the surrounding environment, changing the units of overall oxidation rate constant k to $M^{-2}atm^{-1}s^{-1}$. It must be mentioned that the second-order dependency of the oxidation rate on the pH (as shown in Eq. (5)) was empirically derived out of fitting experimental data between pH 4 and 6 (Morgan and Lahav, 2007), and was further confirmed and extended by Millero (Millero et al., 1987) for oxidation of ferrous ions in solutions ranging from pH 4 to 8. On the other hand, in acidic solutions ($\text{pH} < 4$) and slightly alkaline solutions ($\text{pH} > 8$), the rate of Fe(II) was found to be independent of pH. Therefore, the exponent on the $[OH^-]$ parameter in Eq. (5), changes as a function of pH. Even for the case of near-neutral conditions, the second order dependency has been found to be lower than 2 (precisely between 1.01 and 1.84) by several authors, and is strongly influenced by the anions present in solution (Roekens and Van Greiken, 1984; Lowson, 1982). Millero (1985) explained the pH dependency of the oxidation kinetics with the speciation and hydrolysis of Fe(II) in solution as a function of the pH and showed that the oxidation of iron in the presence of atmospheric oxygen proceeds by a series of parallel reactions with different Fe(II) species as the reactants.

For a given pH and excess O_2 (equilibrium with atmospheric oxygen), Eq. (5) can be written as a pseudo first-order equation w.r.t the total [Fe(II)] (Eq. (6)):

$$\frac{dFe(II)}{dt} = -k_1[Fe(II)] \quad (6)$$

where, k_1 (s^{-1}) is the rate constant for the pseudo first-order reaction w.r.t. [Fe(II)]. Depending on the hydrolysis and speciation of Fe(II), Eq. (6) can be re-written as Eq. (7) (Millero et al., 1987):

$$\frac{dFe(II)}{dt} = -k_1[Fe(II)] = k_a[Fe^{2+}] + k_b[FeOH^+] + k_c[Fe(OH)_2^0] + \dots \quad (7)$$

where, k_a , k_b , and k_c , are the individual rate constants for different Fe(II) species as shown in Eq. 7. Several researchers (King et al., 1995; Santana-Casiano et al., 2004, 2005, 2006) have tried to model the oxidation kinetics of ferrous ions in sea water or carbonate bearing waters based on the individual oxidation rate constant for various Fe(II) species, however, the large number of unknown rate constants and the discrepancies in the rate constants of the individual Fe(II) species reported in the literature (Santana-Casiano et al., 2004, 2006; Whitney King, 1998; Pullin and Cabaniss, 2003), makes the models highly inaccurate and applicable only to the experimental conditions used in a particular study. A simpler kinetic model proposed by Rose and Waite (2002), considers all Fe(II) species as one single entity and all Fe(III) species as one entity. This model does not require prior knowledge of Fe(II) and Fe(III) species at any pH and requires fewer unknown variables, however, it fails to explain the oxidation mechanism.

Whilst there has been significant research in solutions representative of sea water and fresh water in the presence of atmospheric oxygen, there hasn't been much attention paid to the oxidation behaviour of Fe(II) in conditions of lower ionic strength and in the absence of oxygen. Anaerobic conditions are extremely relevant today, especially in the case of radioactive waste disposal and steel corrosion in reinforced concrete infrastructure, and therefore, attention must be paid to thoroughly understand the oxidation behaviour of ferrous ions in such environments. Therefore, this work focusses on the oxidation of ferrous ions in solutions in the near neutral pH, between ~ 5 and ~ 9 . Here, we

Table 1

The initial estimated concentration of various species in solutions tested when 'AA buffer' was used to experimentally measure Fe(II) oxidation. Based on the dilutions performed for each experiment, the estimated concentrations are prior to any addition of FZ1 solution. The ionic strength of the solution is calculated based on all the concentrations of all the ions present (including H^+ from 0.01 M HCl in the stock solution) in solution.

| pH | Fe(II) (M) | Cl (M) | CH ₃ COONH ₄ (M) | Ionic Strength |
|------|-----------------------|-----------|--|----------------|
| 4.92 | 1.99×10^{-5} | 0.0100398 | 0.01892807 | 0.02899 |
| 6.6 | 1.99×10^{-5} | 0.0100398 | 0.04165014 | 0.05171 |
| 8 | 1.99×10^{-5} | 0.0100398 | 0.04656231 | 0.05662 |
| 8.91 | 4.63×10^{-6} | 0.0100093 | 0.37037037 | 0.38038 |

assess the oxidation behaviour of ferrous ions under aerobic and anaerobic conditions, by colorimetric means using a UV-Vis spectrometry. Additionally, the influence of different pH buffers, commonly used in the literature, on the oxidation behaviour is also investigated, as buffers can form complexes with Fe(II) and Fe(III) and thus significantly influence the oxidation rate.

2. Experimental programme

2.1. Materials and solution preparation

All solutions were prepared using Ultrapure water (Milli-Q water, 18.2 M Ω cm resistance) generated by a Milli-Q Gradient A10 purification system (Millipore, USA). The Ultrapure water was deoxygenated by sealed boiling at 230 °C (using a heating plate) for 2 h under continuous purging with N₂ (g) and constant stirring at 450 rpm (similar procedure followed by (Mancini et al., 2020)). The dissolved oxygen concentration in the water was measured by means of PreSens PST6 planar oxygen sensor (Regensburg, Germany) and was found to be below the detection limit (<1 ppb) of the sensor. The degassed water was then transferred into a glovebox (MBraun), and allowed to cool down to room temperature and equilibrate with the inert N₂ atmosphere of the glovebox (O₂, CO₂ < 0.1 ppm). All chemicals used in this study were analytical grade and were obtained from Fluka or Merck and were stored within the glovebox to avoid any atmospheric oxidation. A 10⁻² M FeCl₂ stock solution was prepared using a 0.01 M HCl solution at pH 2. The pH of the stock solution was designed to be low, as the oxidation rate of Fe²⁺ in acidic solutions is extremely slow; and the concentration of Fe²⁺ in a solution of pH 2 was found to be stable over a time-span of 3–4 weeks. The pH of all solutions was measured using a Metrohm combined glass pH electrode and monitored using the Metrohm 781 pH/ion meter, calibrated using NIST buffers with pH 4.01, 7.01 and 10.01. In this study, a ferrozine solution (FZ) was used as the colouring agent to measure the Fe(II) (aq) concentration colorimetrically. FZ is known to react extremely quickly with Fe(II) (aq) (Thompson and Mottola, 1984; Lin and Kester, 1992) to form a stable purple-coloured complex with maximum absorbance at 562 nm and a molar absorptivity of 30,000 Lmol⁻¹cm⁻¹ (Stokey, 1970; Viollier et al., 2000). It is also well known

Table 2

The initial estimated concentration of various species in solutions tested when 'non-complexing' buffers were used to experimentally measure Fe(II) oxidation. These estimated concentrations, calculated based on the series of dilutions for each experiment, are prior to any addition of FZ1/FZ2 solution. The ionic strength of the solution is calculated based on all the concentrations of all the ions present (including H^+ from 0.01 M HCl in the stock solution) in solution.

| pH | Fe(II) (M) | Cl (M) | CH ₃ COONa (M) | HEPES (M) | Na ₂ B ₄ O ₇ ·10H ₂ O (M) | Ionic Strength |
|----|--------------------|----------------------|---------------------------|-----------|---|----------------|
| 5 | 2×10^{-5} | 6×10^{-5} | 0.001 | – | – | 0.00108 |
| 7 | 2×10^{-5} | 6×10^{-5} | – | 0.001 | – | 0.00108 |
| 8 | 2×10^{-5} | 6×10^{-5} | – | 0.001 | – | 0.00108 |
| 9 | 5×10^{-6} | 1.5×10^{-5} | – | – | 0.001 | 0.00302 |

that the interaction of FZ with Fe³⁺ is negligible (Pullin and Cabanis, 2003). Ferrozine solutions were prepared by dissolving 0.01 M of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid, monosodium salt hydrate in deoxygenated water with (FZ1) and without (FZ2) 0.1 M ammonium acetate.

2.2. Oxidation experiments in the 'absence' of oxygen

In a first set of experiments, the stock solution of 10⁻² M FeCl₂ of pH 2 was diluted to concentrations below the solubility limit of Fe(OH)₂ to 2×10^{-5} M for experiments at pH 5, 7, and 8, and to 5×10^{-6} M for experiments at pH 9 (Figure S3). To 50 ml of the diluted FeCl₂ solution at pH 2, 0.19 ml, 0.42 ml, 0.47 ml and 4 ml of a buffer solution of 5 M ammonium acetate (CH₃COONH₄) and ammonium hydroxide (NH₄OH) – referred to as the 'AA buffer' hereafter – with pH 9.5 were added to achieve the desired pH of 5, 7, 8 and 9, respectively. However, the initial measured pH of the solutions was 4.92, 6.6, 8 and 8.91, respectively, instead. The initial concentrations (C₀) of Fe(II) were therefore, lower than those mentioned above. Table 1 shows the initial concentrations of different species in solutions. These solutions were labelled as FeIIox_AA – 5, 7, 8 and 9, corresponding to the pH of the solution. An aliquot of known volume was withdrawn from FeIIox_AA – 5, 7, 8 and 9 after different times and pipetted into a centrifuge tube containing FZ1 and allowed to react with FZ1 for 7–10 min. These solutions were then transferred to a 5 cm quartz cuvette and the absorbance of each of the solutions was measured with the spectrophotometer.

A second set of experiments, solutions at pH 5, 7, 8 and 9 were prepared by adding appropriate aliquots of 0.1 M NaOH or 0.1 M HCl to solutions containing 1 mM of buffer (with appropriate pK_a values) inside the glovebox. In this study, we used sodium acetate (CH₃COONa) for pH 5 solution, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) for pH 7 and 8 solutions, and sodium tetraborate decahydrate for pH 9 solution. It is to be noted that trisaminomethane (TRIS) and N-Cyclohexyl-2-aminoethanesulfonic acid (CHES) were also preliminarily tested for their suitability to buffer solutions at pH 9 without interacting with Fe(II) (aq) (Bradbury and Baeyens, 1999; Chen et al., 2022). These preliminary experiments showed that both CHES and TIRS influence the oxidation of Fe(II) (aq) (Supplementary Information - Figure S1), and hence, these two buffers were rejected. Aliquots of known volume were drawn from the stock 10⁻² M FeCl₂ solution and pipetted into the buffer solutions to achieve an initial concentration (C₀) below the solubility limit w.r.t Fe(OH)₂ at the corresponding pH (Figure S3). In the case of solutions with pH 5, 7 and 8, the initial Fe²⁺ concentration was 2×10^{-5} M, whereas in the case of solution with pH 9, the initial concentration was 5×10^{-6} M. The initial concentration of the studied solutions is shown in Table 2. These solutions were labelled as FeIIox-5, 7, 8 and 9, corresponding to the pH of the solution. An aliquot of known volume was drawn from FeIIox – 5, 7, 8 and 9 at different times and pipetted to a centrifuge tube containing FZ1 and FZ2 and allowed to react with FZ1 and FZ2 for 7–10 min. These solutions were then transferred to a 5 cm quartz cuvette and the absorbance of each of the solutions was measured with the spectrophotometer. Experiments for pH 8 and 9, were also repeated in aluminium foil coated beakers to eliminate the influence of

ambient light on the oxidation behaviour of Fe(II) (aq) (Supplementary Information Figure S2). Preliminary results for experiments in the absence of ambient light showed no or negligible influence of ambient light.

2.3. Oxidation experiments in the 'presence' of oxygen

Specific experiments similar to the second set with sodium acetate, HEPES, and sodium tetraborate decahydrate as buffers for pH 5, 7 and 8, and 9 solutions, respectively, were designed to allow for measuring Fe²⁺ (aq) in the presence of oxygen. Solutions buffered at pH 5, 7, 8 and 9 with the above-mentioned buffers were prepared with ultrapure water (without degassing) outside the glovebox. The solutions were assumed to be in equilibrium with atmospheric oxygen. The stock 10⁻² M FeCl₂ solution was taken out of the glovebox in a sealed Teflon container and a well-defined volume was immediately pipetted into the buffer solutions to achieve the same initial concentrations as mentioned in the second set of experiments. These solutions were labelled as FeIIxO2 - 5, 7, 8 and 9, corresponding to the pH of the solution. An aliquot of known volume was drawn from FeIIxO2 - 5, 7, 8 and 9 after different times and pipetted into a centrifuge tube containing FZ2 and allowed to react with FZ2 for 7–10 min, and then transferred into 5 cm quartz cuvettes to be measured for absorbance by the spectrophotometer.

2.4. Methods

The concentration of Fe²⁺ in the solutions prepared with FZ was measured colorimetrically at a wavelength of 562 nm in a 5 cm quartz cuvette, by means of a Cary 6000i spectrophotometer (Agilent, USA) (Stookey, 1970). Calibration curves were generated for different concentrations of Fe²⁺ (aq) varying between 0 and $\sim 2 \times 10^{-5}$ M in a solution of 0.01 M HCl at pH 2. With the 5 cm quartz cuvette, the detection limit of the spectrophotometer was in the range of $\sim 5 \times 10^{-8}$ M and $2 \times$

10⁻⁵ M. Additionally, the calibration curves were confirmed by following a similar procedure proposed for Fe³⁺ by Viollier et al. (2000). Fig. 1 shows the calibration curve obtained for Fe²⁺ over different concentrations, reduced Fe³⁺ over different concentrations, and the interaction of Fe³⁺ with FZ. The spectrophotometer was zeroed against a baseline measurement of Milli-Q water at 562 nm before each measurement. Additionally, a control specimen containing only the background buffer solution and ferrozine (no iron) was treated as blank, against which all measured absorbance were normalised.

3. Results

Fig. 2 shows the measured Fe(II) (aq) concentrations over time (C_t) in deoxygenated solutions of pH 4.91, 6.6, 8, 8.91 when 'AA buffer' was used. The concentration measured at time ($t = 0$), is the initial concentration (C_0) without the buffer. In the case of solutions at pH 4.91 and 6.6, Fe(II) (aq) was found to decrease extremely slowly over the duration of the experiment, and the half-life was approximately 38,000 min and 3850 min, respectively. In the case of pH 8, Fe(II) (aq) decreased over time relatively quickly and the half-life of Fe(II) (aq) in a solution of pH 8 was observed to be roughly ~ 38 min. In solutions with pH 8.91, Fe(II) (aq) decreased extremely quickly and the half-life was found to be around ~ 2 min. One must note the extremely high standard deviations observed for very low concentrations of Fe(II) (aq), particularly at longer durations during the course of each experiment, especially in the case of pH 8 and 8.91 solutions. Reasons for the higher uncertainty in these experiments will be discussed later in Section 4.1.

A second set of experiments were carried out in the absence of 'AA buffer' to assess the influence of ammonium acetate on the oxidation behaviour of Fe(II) (aq). These experiments were carried out with a set of inert buffers (as mentioned in Section 2) that are known to not form (or form weak) complexes with Fe(II) (aq). The concentration of these buffers was fixed concentration at 1 mM. Fig. 3A and B show the measured [Fe(II) (aq)] at time t , w.r.t. C_0 , in solutions buffered at pH 5, 7, 8 and 9, when the FZ solution was prepared without (FZ2) and with

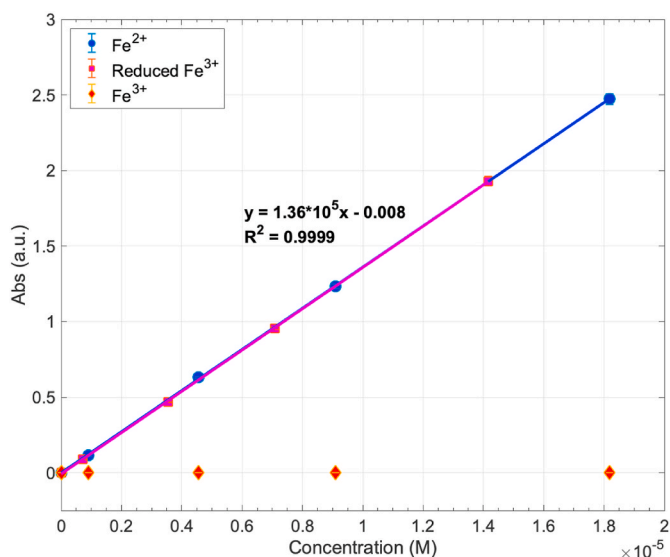


Fig. 1. Calibration curves obtained for different concentrations of Fe²⁺ and Fe³⁺ (reduced with hydroxylamine hydrochloride) for Cary 6000i spectrophotometer, using a 5 cm quartz cuvette. The measured absorbance refers to the absorption of light by the Fe²⁺-FZ complex formed in solution. Additionally, the absorbance in solutions containing Fe³⁺ and FZ was found to be equal to the blank measurement and therefore, it can be confidently ascertained that Fe³⁺ does not form a complex with FZ over the course of the experiment. Data points and error bars represent the mean and standard deviation of triplicate measurements.

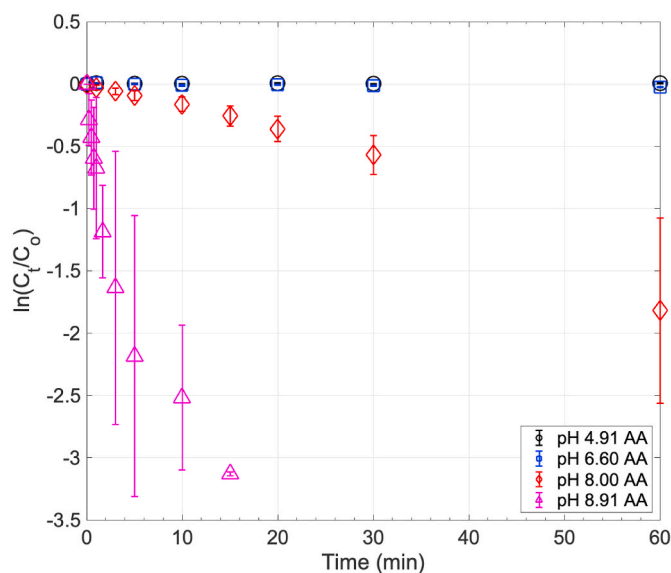


Fig. 2. Measured aqueous Fe(II) concentrations (C_t) in buffered solutions of pH 4.91, 6.60, 8 and 8.91, as a function of time, when FZ1 is used and in anaerobic conditions (dissolved oxygen concentration is $\sim 1.4 \times 10^{-10}$ mol/L). The concentration at time, $t = 0$, refers to the initial Fe(II) concentration (C_0) at the time of dilution. The buffer used in these experiments was the 'AA buffer' (a solution of pH 9.5 consisting of 5 M ammonium acetate (NH₄CH₃CO₂) and ammonium hydroxide (NH₄OH)).

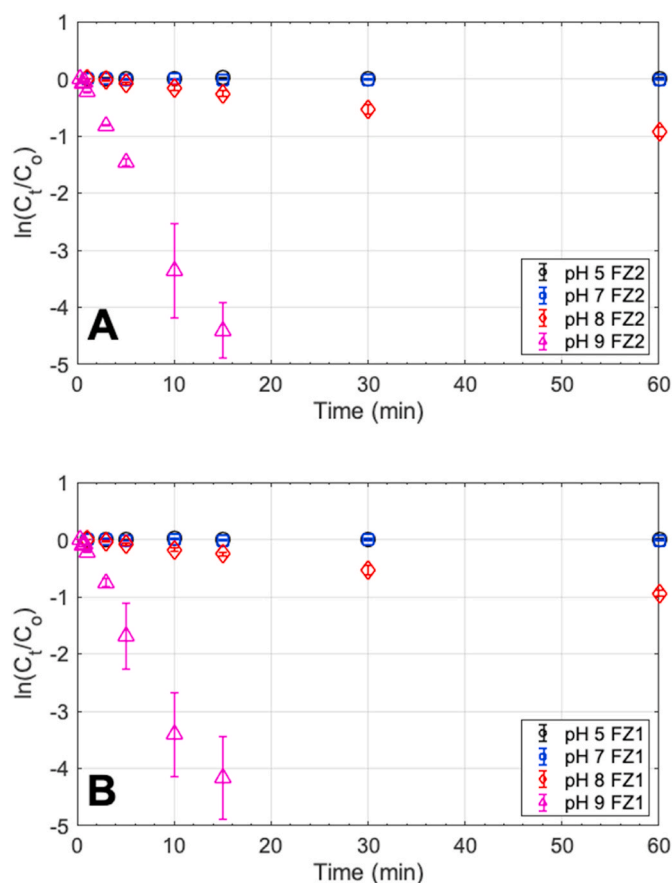


Fig. 3. Measured aqueous Fe(II) concentrations (C_t) in buffered solutions of pH 5, 7, 8 and 9, as a function of time, and when (A) FZ2 and (B) FZ1 are used and under anaerobic conditions (dissolved oxygen concentration is $\sim 1.4 \times 10^{-10}$ mol/L). The concentration at time, $t = 0$, refers to the initial Fe(II) concentration (C_0) at the time of dilution. The buffers used in this experiment were: 1 mM sodium acetate (CH_3COONa) for pH 5; 1 mM N-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES) for pH 7 and 8; and 1 mM sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).

0.1 M ammonium acetate (FZ1), respectively. Fig. 3A shows very similar oxidation behaviour, as seen in Fig. 2. At pH 5 and 7, the measured [Fe(II) (aq)] decreased slowly; and in the case of pH 8 and 9, the half-life of Fe(II) (aq) was also found to be ~ 38 min and ~ 2 min, respectively. One of the major differences in Figs. 3A, 2 and 3B, is that the reproducibility in the experiments without ammonium acetate (Fig. 3A) was much higher, particularly at pH 9, than in the experiments carried out in the presence of ammonium acetate (Figs. 2 and 3B). This observation suggests that the acetate anion does influence the oxidation behaviour of Fe(II).

Fig. 4 shows the measured Fe(II) (aq) in solutions with pH 5, 7, 8 and 9 under aerobic conditions (when all solutions were equilibrated with atmospheric oxygen), when FZ2 is used as the colouring agent. As expected, the decrease in Fe(II) concentration over time was much quicker for experiments conducted at all pH, in comparison to solutions under anaerobic conditions. The half-life of Fe(II) (aq) was found to be ~ 289 min, ~ 58 min, ~ 4.5 min and ~ 0.2 min for solutions at pH 5, 7, 8 and 9, respectively.

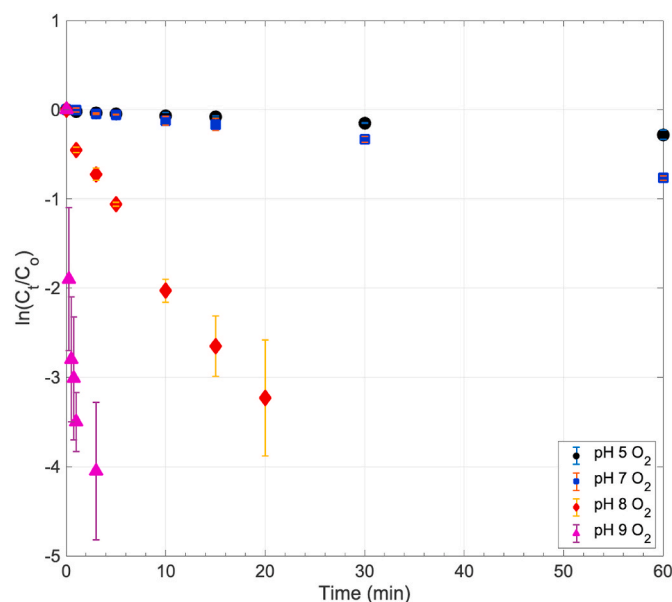


Fig. 4. Measured aqueous Fe(II) concentrations (C_t) in buffered solutions of pH 5, 7, 8 and 9, as a function of time and in the presence of dissolved oxygen, ~ 0.29 mmol/L, (equilibrium with atmospheric oxygen), and when FZ2 is used. The concentration at time, $t = 0$, refers to the initial Fe(II) concentration (C_0) at the time of dilution. The buffers used in this experiment were: 1 mM sodium acetate (CH_3COONa) for pH 5; 1 mM N-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES) for pH 7 and 8; and 1 mM sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).

4. Discussion

4.1. Influence of buffers

For studies in near-neutral pH solutions, the use of suitable buffers is critical. Whilst maintaining a constant pH, it is also significantly important that the buffer does not interact with the ion under consideration (Fe(II) and Fe(III) species in this study) and influences the oxidation at a given pH. Fig. 5 replots data from Figs. 2 and 3A (anaerobic conditions), and compares the oxidation behaviour of Fe(II) when experimental solutions are buffered at pH 6.6, 8 and 8.91 with 'AA buffer'; with the oxidation behaviour of Fe(II) when experimental solutions are buffered with 1 mM of HEPES to achieve pH 7 and 8, and 1 mM of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to achieve pH 9. The discussion presented in the following paragraphs on the possible influence of buffers on the oxidation of Fe(II) is restricted to the experiments carried out under anaerobic conditions and at pH 7, 8 and 9. The influence of 'AA buffer' and 1 mM CH_3COONa on Fe(II) oxidation in solutions at pH 5 are discussed in the Supplementary Information Section 4 and Figure S5.

In the case of pH 7 and 8, there is no significant difference in the oxidation behaviour when either 'AA buffer' or HEPES (as shown in Fig. 5A) are used. The concentration of 'AA buffer' used in both these solutions was roughly the same and around ~ 40 – 46 mM, whereas the concentration of HEPES was 1 mM. In an extensive review by Ferreira et al. (2015) on the suitability or unsuitability of "Good's" buffers (HEPES being one of them) for such studies, HEPES was found to be a non-complexing buffer and thus suitable to be used in solutions with bivalent metal cations (Ferreira et al., 2015). Some biological studies (Kirsch et al., 1998; Baker et al., 2007) have reported results questioning the use of HEPES for oxidation studies, as HEPES could potentially oxidise due to the presence of strong oxidants such as H_2O_2 and release

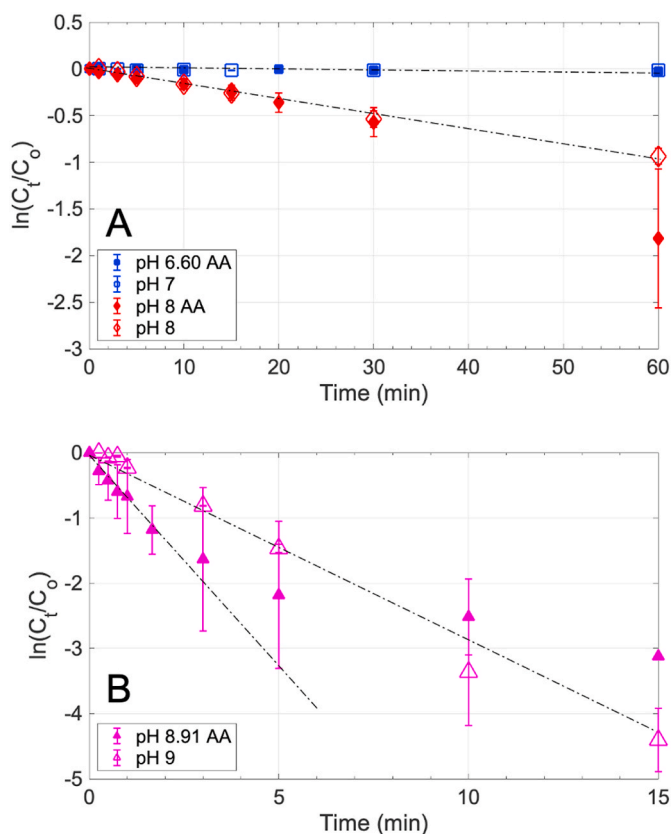


Fig. 5. (A) Comparison between the Fe(II) oxidation results obtained under anaerobic conditions when solutions are buffered with ‘AA buffer’ (pH 6.60, and 8) or HEPES (pH 7 and 8); (B) Comparison between the Fe(II) oxidation results obtained when solutions are buffered with ‘AA buffer’ (pH 8.91) or $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (pH 9). The dashed-dotted lines only serve as a guide to the reader on the linearity or non-linearity in the $\ln(C_t/C_0)$ vs. time plots.

radical cations, which may influence the oxidation behaviour. Tadolini (1987) showed that the oxidation of Fe(II) in solutions buffered with HEPES were not different from that observed in unbuffered solutions. Tadolini (1987) also noted that the kinetics of HEPES oxidation was extremely slow and the timescales of this oxidation reaction is much larger than rate of Fe(II) oxidation in near-neutral to weakly alkaline conditions. Therefore, like other studies (Pham and Waite, 2008; Whitney King, 1998; Pullin and Cabaniss, 2003), the use of HEPES as a non-complexing buffer to study Fe(II) oxidation at pH 7 and 8, was deemed appropriate. Other studies have indicated that at pH 7 or 8, the use of other ‘Good’s’ buffers such as MOPS, TRIS could also be possible (Bradbury and Baeyens, 1999; Chen et al., 2022).

In solutions at pH 8 and at longer durations of the experiment (60 min), the standard deviation increases significantly for ‘AA buffer’ suggesting a higher uncertainty in the measurements at these times. At longer durations (60 min in this study), the higher uncertainty can possibly be attributed to concentrations of Fe(II) being close to the detection limit of the UV–Vis spectrophotometer. Another important factor that could potentially play a role in the higher uncertainty is the complexation of the acetate anion with both Fe(II) and Fe(III). The Fe(III)-acetate complex is more stable than the Fe(II)-acetate complex (Palmer and Hyde, 1993) and could potentially shift the equilibrium towards faster oxidation. Additionally, the higher standard deviation at longer durations of the experiment and for low concentrations of Fe(II), suggest that the acetate anion may also compete with the ferrozine in complexation with Fe(II), possibly resulting in the formation of less stable FZ-Fe(II) complexes. The influence of complexation can also be visualised by the deviation from pseudo first-order kinetics (indicated by

the linear region of the $\ln(C_t/C_0)$ vs. time plot) at longer times in pH 8 solutions, when ‘AA buffer’ is used.

In the case of pH 9 (as seen from Fig. 5B), the uncertainty in the measured absorbance increases as a function of time or a decrease in the Fe(II) concentration, irrespective of the type of buffer used. This can primarily be ascribed to the fact that the concentrations of Fe(II) in the 5 cm quartz cuvette, were close to the detection limit of the UV–Vis spectrophotometer. Still, there are significant differences between results obtained in solutions with ‘AA buffer’ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Fig. 5B). $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ has been extensively employed as a buffer over several decades, in studies (Büchler et al., 1998; Azumi et al., 1987; Pou et al., 1984) concerning the passivation of iron in near-neutral solutions. However, some studies have indicated that the borate anion can adsorb on the surface of passive iron (MacDougall and Bardwell, 1988) and could influence the growth of the passive film. A recent study, pointed out that the borate anion can in fact form complexes with Fe(II) but the kinetics of complexation were found to be extremely slow (Xiong et al., 2018). Therefore, for all practical purposes and the experimental duration of this study, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ can be considered as a non-complexing buffer and does not influence the oxidation behaviour of Fe(II).

Two major observations can be made from Fig. 5B, a) the level of uncertainty in the measurements when ‘AA buffer’ is used is significantly higher when compared to the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ buffer, especially at longer durations of the experiment or when the concentration of Fe(II) is low; and b) the first-order dependency on [Fe(II)] (indicated by the linear region of the $\ln(C_t/C_0)$ vs time plot) does not hold at longer durations of the experiment when ‘AA buffer’ is used. At pH 9, the concentration of acetate anion in solutions (when ‘AA buffer’ is used) is significantly higher (shown in Table 1) than the [Fe(II)] and $[\text{Cl}^-]$. At such a high concentration of acetate anions and low concentrations of Fe(II) in solutions at pH 9, one may not be able to rule out competition between ferrozine and acetate anions for complexation with Fe(II), possibly resulting in less stable FZ-Fe(II) complexes and increasing the uncertainties in the measurements. At this pH, the hydroxide ion also competes for the Fe(II) (due to the hydrolysis of Fe(II) as a function of pH and its influence on oxidation is addressed later in detail). It can only be speculated at this moment, that the higher uncertainty in the measurements in pH 9 solutions with ‘AA buffer’ compared to those with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ are either due to complexation of the acetate anion with Fe(II) and Fe(III) at the acetate concentrations used for pH 9 solutions, or due to minor differences during experimentation such as mixing (or shaking), time of extraction of solutions, especially for such short durations of measuring absorbance, or due to heterogeneous oxidation.

In this study, it is assumed that the oxidation of Fe(II) ions in solution is homogeneous in nature, i.e. aqueous Fe(II) ions oxidise to form aqueous Fe(III) ions. As was explained by Lowson (1982) and Tamura et al., 1976, 1980, this assumption may not be true in near-neutral conditions (especially for pH 7–9) where the solubility of Fe(III) is roughly 2–3 orders of magnitude lower than Fe(II) (Figure S3). Therefore, during the course of Fe(II) oxidation, some Fe(III) ions may form colloids or precipitate as solids. The surface of colloidal particles and precipitates can act as adsorption sites for aqueous Fe(II) and influence the kinetics of oxidation. Tamura et al. (1980) showed that the adsorption of Fe(II) on various Fe(III) oxyhydroxides is extremely rapid and varies for different Fe(III) oxyhydroxides. Additionally, the oxidation of adsorbed Fe(II) occurs alongside the oxidation of aqueous Fe(II).

As shown above, the use of ‘AA buffer’ may not be appropriate for pH above 7 in the experimental durations considered in this study. Therefore, the following sections only consider the cases where sodium acetate (1 mM), HEPES (1 mM) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (1 mM) are used as buffers to achieve a pH of 5, 7 and 8, and 9, respectively.

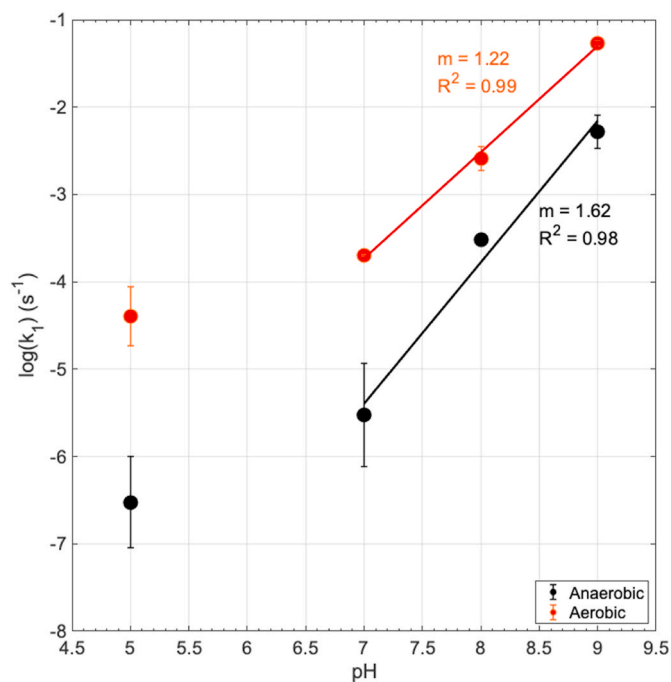


Fig. 6. Pseudo first-order kinetics (k_1) for the oxidation of Fe(II) as a function of the pH of the solution under anaerobic and aerobic conditions and with non-complexing buffers (CH_3COONa for pH 5, HEPES for pH 7 and 8, and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ for pH 9). The pseudo first-order kinetics were estimated (Eq. (6)) by linear fitting the $\ln(C_t/C_0)$ vs. time plots as shown in Fig. 3A (Anaerobic) and Fig. 4 (Aerobic). The values (or slope of $\log(k_1)$ vs. pH) of m (for solutions with pH between 7 and 9), 1.22 ± 0.01 and 1.62 ± 0.03 for aerobic and anaerobic conditions, respectively, represent the order of dependency of k_1 on the $[\text{OH}^-]$ or the pH, as highlighted by Eq. (5). These values of m deviate significantly from the conventionally assumed value of 2.

4.2. Influence of pH and iron speciation

In general, the oxidation rate of Fe(II) in both anaerobic and aerobic conditions was observed to increase with an increase in the pH (as shown by the pseudo first-order rate constant (k_1) vs. pH plot in Fig. 6). The pseudo first-order rate constants (k_1) obtained from the fitting of $\ln(C_t/C_0)$ vs. time plots shown in Fig. 3A (Anaerobic conditions) and Fig. 4 (Aerobic conditions) have also been tabulated in the Supplementary Information (Table S1).

This rapid increase in the oxidation kinetics with increasing pH has been attributed (Stumm, 1990; Luther and Stumm, 1990) to the changes in the speciation of Fe(II) and the fact that hydrolysed Fe(II) species such as FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$ are more readily oxidised than their non-hydrolysed counterparts such as Fe^{2+} . This could be due to the fact that OH^- ligands donate electron density to the Fe(II), resulting in enhanced electron transfer, and thereby stabilising the Fe(III) species formed during oxidation (Stumm, 1990; Luther and Stumm, 1990). Several authors (Millero et al., 1987; King et al., 1995; Santana-Casiano et al., 2004, 2005, 2006) have tried to establish the rate constants for the oxidation of individual Fe(II) species and found that the rate constants of $\text{Fe}(\text{OH})_2(\text{aq})$ was five orders of magnitude higher than the rate constant for FeOH^+ , which in turn was five orders of magnitude greater than the non-hydrolysed Fe(II) species. It is therefore important that we consider the speciation of aqueous Fe(II) ions present in solutions at pH 5, 7, 8 and 9, and in the absence of other anions such as CO_3^{2-} , SO_4^{2-} and Cl^- . Based on the work of Furcas et al. (2022) and Figure S4A, the predominant Fe(II) species present in the solution at pH 5 is Fe^{2+} and the concentrations of other hydrolysed (FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$) are 7–8 orders of magnitude lower. Upon an increase in pH from 5 to 7, 8 and 9, the predominant Fe(II) aqueous species is still Fe^{2+} , however, the molar

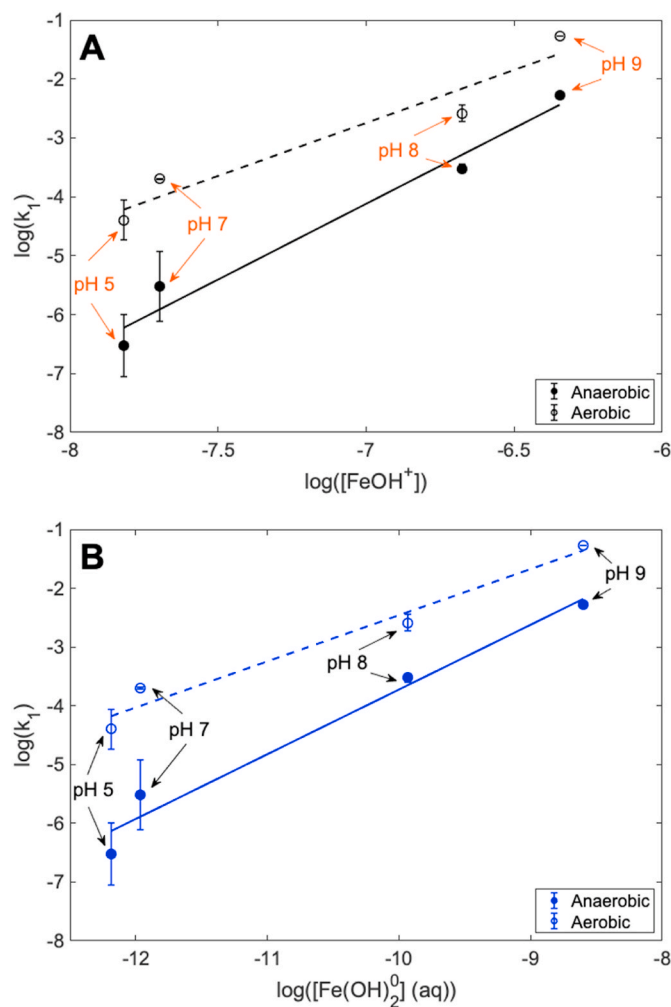


Fig. 7. The dependency of pseudo first-order kinetics (k_1) on the initial (A) $[\text{FeOH}^+]$ and (B) $[\text{Fe}(\text{OH})_2(\text{aq})]$ at pH 5, 7, 8 and 9. The initial concentrations of FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$ were calculated from (Furcas et al., 2022).

fractions of hydrolysed species such as FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$ increase with the pH (Furcas et al., 2022). Fig. 7A and B show plots of the overall pseudo first-order kinetics vs. the initial concentrations (Furcas et al., 2022) of FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$ species, respectively, present in the solutions at pH 5, 7, 8 and 9. The initial concentrations of FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$ at pH 5, 7, 8 and 9 were estimated based on the molar fractions of individual Fe(II) species (Figure S4A) and by assuming instantaneous equilibrium w.r.t. Fe(II) speciation for any given pH. The results agree with the kinetic model proposed by Millero (1985) and King (King et al., 1995), where, the overall pseudo first-order kinetics depend linearly on the molar fractions of different hydrolysed Fe(II) species in solution (Eq. 7). An interesting observation here is that, whilst this relationship for aerobic conditions is well known (Millero, 1985) and satisfied with the results of this study, it is also true for the results in anaerobic conditions. This is indicative of the fact that irrespective of the concentration of dissolved oxygen species, the dependency of the oxidation rate of Fe(II) on the pH is strongly influenced by the molar fractions of various Fe(II) species in solution; and higher concentrations (or molar fractions) of hydrolysed Fe(II) species yield faster oxidation of Fe(II).

Additionally, the solubility of Fe(III) (Figure S3) in pH 5 solutions is much higher when compared to solutions with pH 7, 8 and 9 (Furcas et al., 2022). Therefore, any superoxide formed during the oxidation of Fe(II) can be consumed by soluble Fe(III) and reduced back to Fe(II) (as shown by the reversible reaction in Eq. (1)), lowering the overall

oxidation kinetics in oxygenated solutions with a lower pH. Under anaerobic conditions, a slower oxidation kinetics at pH 5, would essentially be due to the fact that the oxidation rate of Fe^{2+} (predominant species) is extremely slow. Unlike the observation of constant oxidation kinetics for solutions with $\text{pH} > 8$ or 8.5 (Morgan and Lahav, 2007), the oxidation kinetics observed in this study for both aerobic and anaerobic conditions was still influenced by the pH and continued to increase above $\text{pH} > 8$. Such behaviour can be simply explained by the increasing molar fractions of hydrolysed Fe(II) species as the pH of the solution increases from 7 to 9 (Furcas et al., 2022).

4.3. Aerobic conditions

Fig. 6 compares the pseudo first-order rate constant, k_1 , obtained in this study for Fe(II) oxidation in the presence of oxygen (large filled black dots) with reported literature values (Stumm and Lee, 1961; Millero et al., 1987; Pham and Waite, 2008; Emmenegger et al., 1998; Roekens and Van Greiken, 1984; Stumm, 1990; Santana-Casiano et al., 2005; Pullin and Cabaniss, 2003; Shigematsu et al., 1976) as a function of pH, and highlights the dependency of the pseudo first-order rate constant (obtained in this study in solutions with pH between 7 and 9 – black solid line) on the pH of the studied solution. Values of k_1 in oxygenated solutions at each pH were derived by linearly fitting (Eq. (6)) the $\ln(C_t/C_0)$ vs. time plot shown in Fig. 4.

As seen in Fig. 8, k_1 obtained for solutions at pH 7, 8 and 9 in our study agree well with those reported in the literature. Whilst k_1 is known to increase with the pH (Millero et al., 1987), the majority of the studies in the literature report a second-order dependency on the pH (Eq. (3)), especially in near-neutral conditions (Stumm and Lee, 1961; Emmenegger et al., 1998). However, this reported second-order dependency is in fact merely an approximation, and varies between 1.01 and 2.29 (Stumm and Lee, 1961; Millero et al., 1987; Pham and Waite, 2008;

Emmenegger et al., 1998; Roekens and Van Greiken, 1984; Stumm, 1990; Santana-Casiano et al., 2005; Pullin and Cabaniss, 2003; Shigematsu et al., 1976) and is strongly influenced by different experimental variables such as ionic strength, other anions, temperature and dissolved oxygen concentration. In our study, this dependency was found not to be second-order w.r.t. pH and instead an exponent of 1.22 (for the $[\text{OH}^-]$ term in Eq. (3)) for solutions with pH ranging between 7 and 9. This deviation may be explained by the absence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ (as is the case in most studies in the literature) in the solutions studied here. It is well known that in the presence of carbonates in solutions with $\text{pH} > 6$, the concentration of $\text{Fe}(\text{CO}_3)_2^{2-}$ and $\text{Fe}(\text{OH})_2(\text{aq})$ are second-order w.r.t. $[\text{OH}^-]$ and therefore, dominate the overall Fe(II) oxidation kinetics (Pham and Waite, 2008; Santana-Casiano et al., 2004; Whitney King, 1998). Therefore, in the absence of any iron-carbonate complexes, the pseudo first-order oxidation kinetics essentially depends on the molar fractions of $\text{Fe}(\text{OH})_2(\text{aq})$, FeOH^+ and Fe^{2+} . Additionally, the deviation of second-order dependency as a function of the $[\text{OH}^-]$ could also be heterogeneous oxidation of Fe(II) in the presence of Fe(III) oxide/hydroxide colloids or precipitates between pH 7 and 9.

The value of k_1 measured for solutions with pH 5 in this study was roughly two orders of magnitude higher than those observed in other studies. This can be possibly attributed to differences in the ionic strength as well as the absence of chloride/sulfate/bicarbonate ions in solutions in this study, when compared to other studies in the literature. At pH 5.45 in seawater, Roekens et al. (Roekens and Van Greiken, 1984) estimated k_1 to be roughly two orders of magnitude lower than the value reported in our study, and the variation in both the studies is solely due to differences in the concentration of chlorides or salinity. Sung and Morgan (1980) have experimentally observed that an increase in the chloride ion concentration can lead to a reduction in the kinetics of oxidation by two orders of magnitude. Luther (Luther and Stumm, 1990) explained this reduction in oxidation kinetics in the presence of

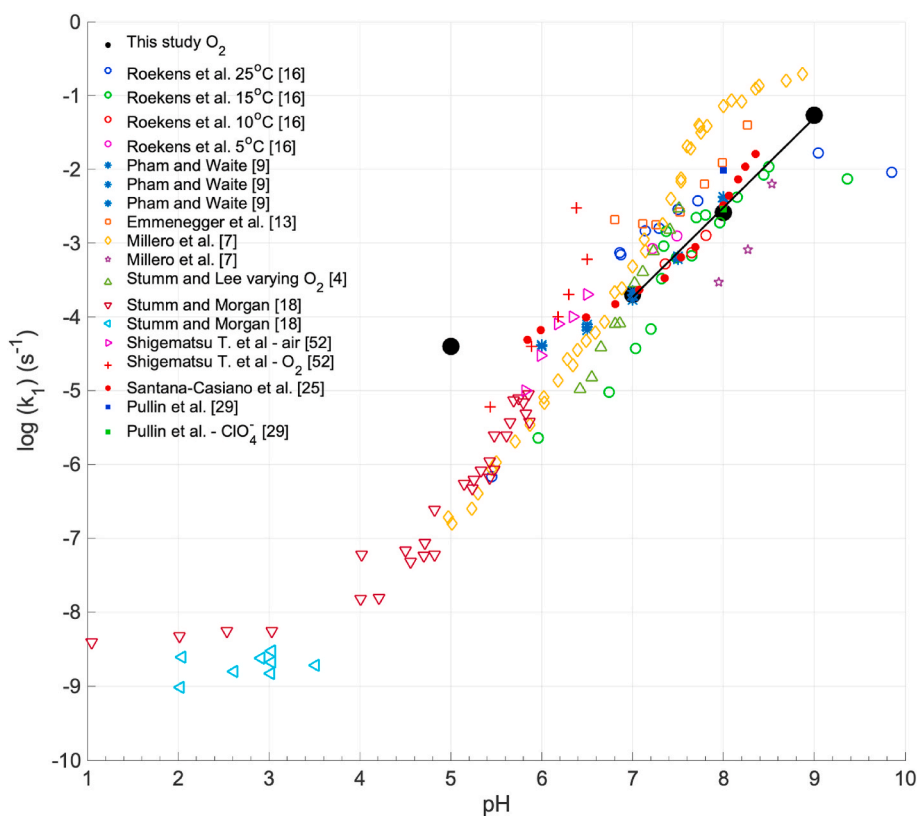


Fig. 8. Pseudo-first order rate constant obtained for the oxidation of Fe(II) in aerated solutions with pH ranging 5 to 9 in this study. Additionally, these rate constants are compared with those reported in the literature (Stumm and Lee, 1961; Millero et al., 1987; Pham and Waite, 2008; Emmenegger et al., 1998; Roekens and Van Greiken, 1984; Stumm, 1990; Santana-Casiano et al., 2005; Pullin and Cabaniss, 2003; Shigematsu et al., 1976).

chlorides due to the formation of Fe(II)–Cl complexes and as chloride is a weak σ donor, the outer-sphere electron transfer process is slower when compared to ferrous oxidation in chloride free solutions. Based on the speciation of Fe(II) in chloride containing solutions ($[\text{Cl}^-] > 0.1 \text{ mol/L}$) (Santana-Casiano et al., 2004; Furcas et al., 2022), it is expected that Fe(II) forms stable aqueous chloride complexes at pH 5. This could explain the observation of a significantly higher rate of oxidation in this study for solutions buffered at pH 5 with negligible concentrations of Cl^- , in comparison to kinetic rate constants reported in the literature where Fe(II) oxidation behaviour was monitored in solutions with $[\text{Cl}^-] > 0.1 \text{ mol/L}$.

4.4. Anaerobic conditions

It is important to draw the attention of the reader to the fact that here ‘Anaerobic conditions’ refer to conditions when the dissolved oxygen concentration in the experimental solution is in equilibrium with the oxygen concentration of the glovebox ($<0.1 \text{ ppm}$), and is around 4–5 orders of magnitude lower than the initial $[\text{Fe(II)}]$. Thus, since the oxygen concentration is so much lower than the initial $[\text{Fe(II)}]$ and since over the course of the experiments the residual oxygen will be rapidly consumed in the electrolyte, we assume that there is negligible oxygen in these experiments and refer to them as experiments under “anaerobic conditions”.

As mentioned earlier, the oxidation of ferrous ions in anaerobic conditions follows the same trend as in aerobic conditions, i.e., increased oxidation rate with increasing pH. At pH 5, the pseudo first-order kinetics under anaerobic conditions is roughly two orders of magnitude lower than aerobic conditions, irrespective of the buffer used. Upon moving from pH 7 to 9, the values of k_1 , still much lower (1–2 orders of magnitude lower) when compared to the ones obtained in aerobic environments, tend to converge with those obtained under aerobic conditions with an increase in the pH, suggesting that maybe the dissolved oxygen is less of an influencing parameter under these conditions, when compared to the speciation of Fe(II) in solution.

There only exists one study in the literature to have investigated the stability of Fe(II) in deoxygenated solutions at the pH of our interest. Mancini et al. (2020) conducted similar experiments in the same glove box and measured $[\text{Fe(II)}]$ as a function of time using the same spectrophotometer. In their work, the desired pH of the solution (7.20, 8.10, and 9.00) was attained by adding only NaOH and HCl. In their experiments, Mancini et al. (2020) observed an induction period, where the Fe(II) concentration remained constant before the commencement of ferrous oxidation. This induction period was found to decrease with an increase in the pH of the solution and was $\sim 300 \text{ min}$ for pH 7.20, $\sim 30 \text{ min}$ for pH 8.10 and $\sim 15 \text{ min}$ for the case of pH 9.00. After the induction period, they reported a similar behaviour of increased oxidation rates with an increase in the pH. As discussed earlier, this behaviour is similar to that observed in this study (Fig. 3) and elsewhere in the literature. An important conclusion that can be drawn from Mancini et al. (2020) is that even in the absence of buffers, the oxidation of Fe(II) is still possible in anaerobic conditions and the oxidation rate increases with a rise in the pH, ruling out any influence of non-complexing buffers (used in this study) on the oxidation of Fe(II).

Whilst it was not explained by Mancini et al. (2020) as to why they observed an induction period, it can be hypothesised that the pH was probably drifting during the course of the experiments. Such a drift in the pH of the solution under unbuffered conditions has been previously observed by especially when only NaOH/HCl are used to achieve near-neutral pH (pH: 5 to 9) solutions (Baeyens and Bradbury, 1995). In this study, such an induction period was not observed and the oxidation of Fe(II) started instantaneously. Additionally, in our preliminary work it was not possible to obtain a constant pH of 7, 8 and 9 within a reasonable timeframe with the method prescribed by Mancini et al. (2020) and therefore, we made use of non (or weak)-complexing pH buffers instead.

4.5. Mechanism of anaerobic Fe(II) oxidation

Whilst the Haber-Weiss mechanism (Weiss, 1935) (Eq. (1) to Eq. (4)) involving intermediate reactive oxygen species explains the mechanism for oxidation of Fe(II) in oxygenated or aerobic conditions, there doesn't exist a mechanism describing the oxidation of Fe(II) in anaerobic conditions. As highlighted above and expected, the absence of oxygen (or the dissolved oxygen concentration ($\sim 1.4 \times 10^{-10} \text{ mol/L}$) being 4 to 5 orders of magnitude lower than the initial $[\text{Fe(II)}]$) lowers the kinetics, but does not inhibit the oxidation of Fe(II). However, as the anodic oxidation of Fe(II) proceeds and forms Fe(III), there must be a species acting as an electron acceptor forming the cathodic reaction of the system, that does not involve dissolved oxygen. There is overwhelming research on the oxidation of Fe(II) in anaerobic conditions in the presence of different bacteria (Bryce et al., 2018), that act as the electron acceptors. However, in the absence of other oxidising agents, as is the case in the experiments conducted in this study, the proposed mechanisms are not applicable. In such conditions, the oxidation of Fe(II) under anaerobic conditions can be viewed by the following anodic (Eq. 7) and cathodic reactions (Eq. (8) for $\text{pH} > 7$ and Eq. (9) for $\text{pH} \leq 7$):



Under anaerobic conditions, for the cathodic reaction to be the hydrogen evolution reaction due to reduction of water (at different pH considered in this study), the reversible potential ($E_{\text{rev, anode}}$) of the anodic reaction needs to be lower than the $E_{\text{rev, cathode}}$ of the cathodic reaction (based on Eq. (10)).

$$\Delta G_{\text{cell}} = -nFE_{\text{rev, cell}} = -nF(E_{\text{rev, cathode}} - E_{\text{rev, anode}}) \quad (10)$$

where, ΔG_{cell} is the Gibbs free energy of the redox cell. As briefly discussed in Section 4.2, the anodic reactions are determined by the thermodynamic stability and molar fractions of hydrolysed and non-hydrolysed Fe(II) species at different pH. Additionally, it is also important to consider the thermodynamic stability of different Fe(III) aqueous species, that form as a result of the oxidation of Fe(II) at any given pH (Figure S4B). At pH 5, Fe(III) species predominantly exist as Fe(OH)_2^+ along with minor quantities of FeOH^{2+} , and $\text{Fe(OH)}_3(\text{aq})$ (Furcas et al., 2022). $\text{Fe(OH)}_3(\text{aq})$ is the predominant species at pH 7 and 8, followed by Fe(OH)_2^+ and some minor quantities of Fe(OH)_4^- (Furcas et al., 2022). At pH 9 though, the Fe(III) aqueous species are constituted of mainly $\text{Fe(OH)}_3(\text{aq})$ and Fe(OH)_4^- (Furcas et al., 2022). At a given pH, Fe(II) ions speciate and are present in solution in different hydrolysed or non-hydrolysed states. The molar fractions of each of the species are governed by the thermodynamics of the system and the anions present ($[\text{OH}^-]$ in this study) in the solution. Fe(II) species oxidise to form the most thermodynamically favoured Fe(III) species in solution. Table 3 enlists the Gibbs free energy of the reactions, at standard conditions, of different Fe(II) species oxidising to different Fe(III) species, calculated from the thermodynamic data reported by Furcas et al. (2022). Based on the molar fractions of various Fe(II) species, the initial concentrations of each of the Fe(II) species listed in Table 3 can be calculated from total concentration of Fe(II) used in the oxidation experiments at pH 5, 7, 8 and 9. Here, we assume that the dissolved oxygen concentration in solution is in equilibrium with the maximum oxygen concentration in the glovebox ($<0.1 \text{ ppm}$), and is roughly 10^{-10} mol/L . Therefore, the $E_{\text{rev, anodes}}$ calculated from the Nernst equation (Eq. 11), of different oxidation reactions assumed that the initial total $[\text{Fe(III)}]$ is 10^{-10} mol/L , and the individual concentrations of each of the Fe(III) species at pH 5, 7, 8 and 9 are calculated from the thermodynamically determined molar fractions of each Fe(III) species. The $E_{\text{rev, anode}}$ for different oxidation reactions are

Table 3

Gibbs free energy changes of oxidation reactions (Δ_rG in kJmol^{-1}) between all Fe(II) and Fe(III) species at standard conditions. The oxidation reactions considered are mentioned in the Supplementary Information. At the pH of our interest (pH: 5 to 9), the molar fraction of $\text{Fe}(\text{OH})_3(\text{aq})$ is always around 10–12 orders of magnitude lower than the predominant Fe^{2+} species (Furcas et al., 2022), and therefore, were not considered.

| Species | Reactants | | | |
|-------------------------------------|------------------|-----------------|-------------------------------------|----------------------------|
| | Fe^{2+} | FeOH^+ | $\text{Fe}(\text{OH})_2(\text{aq})$ | $\text{Fe}(\text{OH})_3^-$ |
| Fe^{3+} | 74.49 | 100.55 | 117.13 | 127.60 |
| FeOH^{2+} | 87.09 | 33.23 | 49.81 | 60.28 |
| $\text{Fe}(\text{OH})_2^+$ | 107.16 | 53.30 | -10.04 | 0.43 |
| $\text{Fe}(\text{OH})_3(\text{aq})$ | 144.58 | 90.72 | 27.38 | -42.07 |
| $\text{Fe}(\text{OH})_4^-$ | 197.93 | 144.07 | 80.73 | 11.28 |

listed in Supplementary Information (Table S2).

$$E_{rev,anode} = E_{anode}^o + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad (11)$$

where, E_{anode}^o is the standard potential (at standard conditions) for the oxidation reaction and calculated by dividing the Gibbs free energy of reaction with the Faraday constant (F) and the value of n being -1 for a single electron transfer process (Eq. (10)).

Based on the $E_{rev,anode}$ calculated using Eq. (11), the anodic reaction at pH 5 proceeds by the oxidation of Fe^{2+} to $\text{Fe}(\text{OH})_3(\text{aq})$, FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$. Similarly at pH 7, the anodic reaction proceeds by the oxidation of Fe^{2+} to FeOH^{2+} , $\text{Fe}(\text{OH})_3(\text{aq})$ and $\text{Fe}(\text{OH})_4^-$; as well as the oxidation of FeOH^+ to $\text{Fe}(\text{OH})_3(\text{aq})$ and $\text{Fe}(\text{OH})_4^-$; and the oxidation of $\text{Fe}(\text{OH})_2(\text{aq})$ to $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_4^-$. At pH 8, Fe^{2+} and FeOH^+ oxidises to $\text{Fe}(\text{OH})_3(\text{aq})$ and $\text{Fe}(\text{OH})_4^-$, whereas $\text{Fe}(\text{OH})_2(\text{aq})$ oxidises to $\text{Fe}(\text{OH})_4^-$. In the case of pH 9, Fe^{2+} undergoes oxidation to form $\text{Fe}(\text{OH})_3(\text{aq})$ and $\text{Fe}(\text{OH})_4^-$; whereas, both FeOH^+ and $\text{Fe}(\text{OH})_2(\text{aq})$ oxidise to form $\text{Fe}(\text{OH})_4^-$. For all the oxidation reactions mentioned above, the $E_{rev,anode}$ (calculated for the abovementioned assumed initial conditions) lies below the reversible potentials of the hydrogen evolution reaction at pH 5, 7, 8 and 9, making the hydrogen evolution reaction the perfect candidate for the cathode under anaerobic conditions. With time, the concentrations of Fe(III) species in solution will increase, until it reaches its solubility limit. Consequentially, the $E_{rev,anode}$ (based on Eq. (11)) would also increase and the driving force ($E_{rev,cathode} - E_{rev,anode}$) of the oxidation reaction will decrease. Therefore, it is expected (and as seen in Figs. 2, Figs. 3 and 4) that initially the oxidation of Fe(II) proceeds at a faster rate and then slows down at later stages of the experiment. Based on the cathodic reactions (Eq. (8) and Eq. (9)) under anaerobic conditions, it could also be supposed that for $\text{pH} > 7$, the OH^- produced during the cathodic reaction undergoes further autoprotolysis to form O_2^- or H_2O_2 (Lee et al., 2019), which are known to be effective oxidants. The concentrations of O_2^- or H_2O_2 formed due to the autoprotolysis of OH^- would linearly scale with the pH of the solution, and be responsible (in addition to the presence of hydrolysed Fe(II) species) for the increase in the oxidation kinetics of Fe(II) with an increase in the pH. The same oxidation reactions would hold true for the case of aerobic conditions as well, but the driving force for each of the reactions would depend on the difference between the $E_{rev,cathode}$, when oxygen or other intermediate oxidising species act as the cathode, and the $E_{rev,anode}$. In the experiments done in this study, the pH of the solution is kept constant over time due to the presence of a buffer, and so during the course of oxidation (and regardless of which anodic reaction occurs) the molar fractions of different hydrolysed or non-hydrolysed Fe(II) and Fe(III) species must remain constant. Therefore, the kinetics of each individual oxidation reaction possible at a given pH is also in competition with the

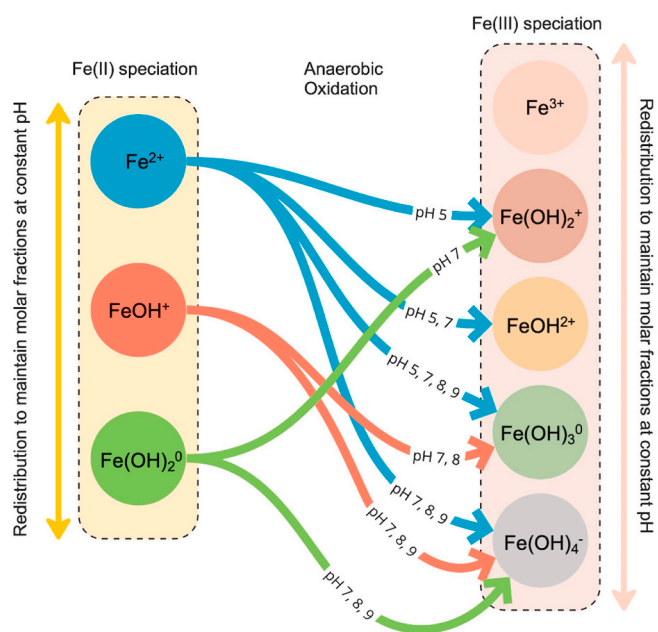


Fig. 9. A schematic representation of the hypothesised mechanism of Fe(II) oxidation under anaerobic conditions.

kinetics of Fe(II) and Fe(III) speciation.

Based on the results obtained in this study and considering the thermodynamics of the Fe(II)–Fe(III)– H_2O systems at different pH, we could hypothesise a mechanism for anaerobic (or when concentration of dissolved oxygen is 4–5 orders of magnitude lower than the initial [Fe(II)]) oxidation of Fe(II). Fig. 9 is a schematic representation of a mechanism hypothesised for the anaerobic oxidation of Fe(II) in solutions of constant pH 5, 7, 8, and 9. Depending on the pH of the solution, Fe(II) speciates and exists in the form of hydrolysed and non-hydrolysed species. As observed experimentally, Fe(II) can oxidise to a higher valence state, namely Fe(III), even in the absence of dissolved oxygen in solution. Unlike oxygenated conditions where the dissolved oxygen acts as the electron acceptor, the reaction that complements the oxidation of Fe(II) is the reduction of H_2O that results in the evolution of $\text{H}_2(\text{g})$. The oxidation of Fe(II) under aerobic and anaerobic conditions cannot be described as a single reaction, instead, is characterised by a series of parallel reactions involving the thermodynamically most stable Fe(II) and the resulting Fe(III) species. Additionally, as the pH is kept constant in this study, aqueous Fe(II) and Fe(III) species, once consumed and

formed over the course of the experiment, respectively, will re-equilibrate (hydrolyse and de-hydrolyse) to maintain the thermodynamically stable molar fractions of each of the Fe(II) and Fe(III) species (according to Figure S4 – Supplementary Information). It must also be noted that the hypothesised mechanism here, would be relevant for any given pH, given one takes into account the speciation of Fe(II) and Fe(III) at the pH of interest. It is also important to mention that the precipitation of Fe(III) solids (due to the low solubility of Fe(III) – as shown in Figure S3), could also influence the overall rate of Fe(II) oxidation in anaerobic conditions.

5. Conclusion

This study investigated both the aerobic and anaerobic oxidation of Fe(II) species in solutions at buffered pH within the pH range 4.91–9. The following major conclusions can be drawn from this study:

1. Under anaerobic conditions, the *mechanism of oxidation* of Fe(II) can be characterised by a set of parallel reactions involving different hydrolysed and non-hydrolysed Fe(II) and Fe(III) species (Fig. 9). This is similar to the mechanism of oxidation described in the literature for aerobic conditions. However, in the absence of oxygen, the cathodic reaction accompanying the anodic oxidation of Fe(II), is the reduction of H₂O (l) releasing H₂ (g). This proposed mechanism was underpinned by thermodynamic considerations taking into account the time- and concentration dependent Gibb's free energies (reversible potentials) of the different possible reactions for various Fe(II) and Fe(III) species. Moreover, thermodynamic considerations suggest that at a given pH, the molar fractions of both Fe(II) and Fe(III) species involved in the oxidation reactions are determined by the thermodynamic stability of different aqueous species. Thus, at a constant pH (buffered) and at any given moment in time during the course of oxidation, Fe(II) and Fe(III) species would re-equilibrate to maintain the molar fractions based on the thermodynamic stability of each species.
2. We observed the oxidation kinetics to be first-order w.r.t. [Fe(II)] in both aerobic and anaerobic conditions. Whilst the oxidation rate of Fe(II) in anaerobic conditions was observed to be much slower than those observed in aerobic conditions, in both the cases, the oxidation rate increased with an increase in the pH of the solution. This was explained by the fact that with an increase in pH, the concentration of hydrolysed Fe(II) species increases and that hydrolysed Fe(II) species (FeOH⁺, Fe(OH)₂ (aq), Fe(OH)₃) oxidise at a much faster rate than Fe²⁺ (aq), primarily due to the fact that OH⁻ ligands can donate electron density to the Fe(II), enabling enhanced electron transfer. This hypothesis was confirmed by the linear relationship between the calculated pseudo first-order kinetics and the initial concentrations of FeOH⁺ and Fe(OH)₂ (aq) in solutions between pH 5 and 9. It should be mentioned that our observation of the rate of Fe(II) oxidation showing first-order dependency w.r.t. [OH⁻] in the pH range 7–9 disagrees with other literature studies, where it is highlighted that the kinetic rate constant of Fe(II) oxidation shows second order dependency w.r.t. [OH⁻] in solutions with pH between 5 and ~8, and becomes independent of the [OH⁻] for pH > 8. This discrepancy can be explained by the differences stemming from experimentation between this study and those in the literature. In particular, these differences are related to the ionic strength of the solutions and the chemical composition (mainly, the absence of anions such as HCO₃⁻, CO₃²⁻ and Cl⁻ that can complex with Fe(II) in this study). Another important point, in regards to the kinetics, is that here we assumed homogeneous oxidation of Fe(II) species that result in the formation of aqueous Fe(III) species. However, given the low solubility of Fe(III) in solutions at pH 7, 8 and 9, the oxidation kinetics would also be influenced by the formation of Fe(III) colloids or precipitates that could act as adsorption/nucleation sites.

3. In this study, CH₃COONa, HEPES and Na₂B₄O₇·10H₂O at a concentration of 1 mM was found to be appropriate to study the oxidation of Fe(II). Whilst a buffer based on ammonium acetate gave similar results when compared to other buffers, its appropriateness may be limited to neutral or acidic solutions. Efficacy of buffers based on the acetate anion in mildly alkaline conditions and when used in high concentrations, may be compromised by strong complexation of the acetate anion with the metallic cation of interest, as shown by Fe(II) in this study.

Credit author statement

Shishir Mundra: Conceptualization, Investigation, Methodology, Validation, Visualization, Formal analysis, Writing – Original Draft, Writing – Review & Editing; Jan Tits: Methodology, Resources, Writing – Review & Editing; Erich Wieland: Conceptualization, Resources, Methodology, Writing – Review & Editing, Supervision, Project administration; Ueli M. Angst: Conceptualization, Writing – Review & Editing, Supervision, Project administration, Validation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.138955>.

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