Ferrate as a sustainable and effective solution to cope with drinking water treatment plants challenges

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Abstract

Surface water quality is declining due to climate change, leading to increased concentrations of soluble metals, natural organic matter (NOM), turbidity, and algal blooms. These changes pose challenges to traditional water treatment plants, needing innovative approaches. Ferrate(VI) was explored as a potential solution to address climate change-related water emergencies, either alone or in combination with conventional reagents to producing potable water.

Results show that Fe(VI) was more effective to remove soluble manganese compared to a conventional oxidant (permanganate), while requiring a lower stoichiometric dosage (<2 mol of Fe(VI) per 3 mol of Mn(II)) as the reaction byproducts of Fe(VI) reduction (eg., Fe^{3+}) contributed to manganese removal. A slightly alkaline environment (pH >8.5) was crucial to maximize manganese oxidation since pH closer to neutral caused the reduction of Fe(VI) to Fe(III), thus decreasing its reduction potential. Fe(VI) was also effective toward NOM although its activation was necessary to provide noticeable effects. In combination to conventional coagulant/flocculant agents, Fe(VI) was able to provide noticeable increases in removal of turbidity (<0.30 NTU) while involving a simultaneous decrease in other chemicals requirement (>50%). Besides, Fe(VI) was also capable of providing algae removal of approximately 80% higher than conventional oxidizing agent, through simultaneous oxidation and flocculation.

This study demonstrated that employing Fe(VI) as a treatment method for drinking water is very promising as it can serve as an alternative or complement conventional approaches in tackling the challenges presented by climate change and sustaining high-quality standard potable water.

Keywords: Algal bloom, Drinking water, Ferrate, Manganese, Turbidity

1. Introduction

The latest Intergovernmental Panel on Climate Change (IPCC) report reveals that climate change is widespread, rapid, and intensifying (Ma et al., 2022). Besides quantitative impacts (e.g., floods and droughts), it is widely recognized that surface water quality is also affected by climate change. A key factor affecting surface water quality is temperature, since it influences physical, chemical and biological processes, as well lake stratification and mixing (Calero Preciado et al., 2021; Malmaeus et al., 2006).

According to a throughout literature review, it arose that the main effects of climate change in terms of water quality impacts are referred to three main concerns: (i) increase of soluble metals (Fe, Mn, Al) which are released from lake sediments under anoxic conditions (Freeman et al., 2017; Jarsjö et al., 2020), (ii) algal bloom due to the increase of water temperature in nutrients rich lakes (Gobler, 2020), (iii) increase of natural organic matter (NOM) concentration and turbidity as a consequence of extreme precipitation events (Hashempour et al., 2020). A large-scale analysis on water quality under droughts and heatwaves confirmed a general worldwide deterioration in river water quality under these extreme events (Graham et al., 2024).

Among metals, manganese is a contaminant of particular concern for the quality of raw water to be treated in drinking water treatment plant. In recent years, several studies have observed abnormal increases in soluble manganese concentrations (Mn^{2+}) in raw water, exhibiting strong seasonality with peaks occurring mainly during autumn and winter (Aiken et al., 2023; DeSimone and Ransom, 2021; Matveeva et al., 2022). These increases may be closely connected to climate change, as variations in certain environmental parameters (temperature, dissolved oxygen, redox potential) can alter the pathways of manganese diffusion in water. A recent study underlined that under the anaerobic conditions, manganese, and other metals can be reduced by methanogenic microorganisms. The formation of sulfidic conditions in an aquifer triggers the reduction of iron and manganese oxides, leading to an increase in the concentrations of Mn^{2+} as well as other elements (Dao et al., 2024). This facilitates its solubilization and transport to water treatment plants, thus posing significant challenges for its removal (Niemistö and Lund-Hansen, 2019). Moreover, under the influence of climate warming, many large lakes have experienced an increase in algal blooms and eutrophication (Jinge Ma et al., 2023). Algal bloom in water reservoir can cause several problems on conventional water treatment including bad taste and odors (Hung and Liu, 2006), so removal of these algal blooms is now a major challenge in the drinking water treatment (V. Karim et al., 2020). Similarly, increase of NOM concentration and high turbidity are often connected to increased precipitation and runoff, as well as more intense and frequent extreme weather events (Sharma, 2020; Skaland et al., 2022). All these changes could represent a risk for drinking water distribution service (Undurraga et al., 2020). Indeed, The poor quality of the water coming into treatment plants makes the purification process more challenging and could led to water service interruption if drinking water standard quality are not ensured (Luh et al., 2015).

Manganese is commonly removed by using strong oxidants that convert soluble manganese (Mn^{2+}) into insoluble (Mn^{4+}) that can be separated through filtration (Tobiason et al., 2016). Removal of NOM in drinking water treatment plant is of particular concern. Although NOM is not toxic, its presence in drinking water sources is highly detrimental because it is an important source of disinfection byproducts (DBP) precursors. Recent studies demonstrated that a key approach for controlling DBP in drinking water is to maximize NOM removal before chlorination (Jiang et al., 2016). To this aim, pre-oxidation is commonly performed to partially oxidize NOM and DBP before clariflocculation process. As regard this point, previous studies reported that strong oxidants (e.g., ozone) may alter the structure and characteristics of NOM, which become more hydrophilic and fragmented and thus impacting its removal by subsequent coagulation/flocculation process (Graham et al., 2010). Algae removal from water is difficult because of their small size and the low specific gravity. Various treatment processes for removing of algae from water have been tested. Typically, pre-oxidation followed by coagulation/flocculation and filtration is the most applied treatment stages for algae removal from drinking water (Kubiňáková et al., 2017). Even in this case, pre-oxidation is a crucial step for algae removal. Indeed, previous studies observed that a decrease of algal cell activity and chlorophyll concentration enhanced the coagulation process (Ma and Liu, 2002). Nevertheless, DBP production poses a substantial ongoing risk and remains a significant threat that demands attention and mitigation efforts.

Based on what above stated, pre-oxidation is a key process for removal of these pollutant from water both because it is necessary for the removal of the specific pollutant and to prevent the formation of byproducts in subsequent downstream treatments. However, conventional oxidants, like ozone (O_3), chlorine compounds (e.g., ClO_2), permanganate (MnO_4^-) might lead to disadvantages among which high production costs and complex onsite generation facilities (ozone), byproducts generation (chlorine compounds) and overproduction of particulate manganese (permanganate) (Jiangya Ma et al., 2023). Furthermore, due to the heterogeneity of

pollutants and the inability to predict in some cases the sudden increase in their concentrations, it is necessary to rely on oxidizing agents capable of acting on a wide range of compounds and being ready for use in any situation.

In this framework, when pollutants concentration in the raw water increase, drinking water treatments using conventional chemicals might not be able to ensure compliance with drinking water quality standards. Such situation could generate malfunctions in drinking water treatment plant and pose high risk for human health (Leveque et al., 2021). Therefore, considering the unpredictable character of climate change and its impacts, ensuring the safety of drinking water in the presence of climate-driven risks will continue to be an ongoing and enduring challenge for drinking water facilities. At present, the risks to drinking water quality are apparent, emphasizing the importance of addressing these emergencies through the exploration of novel treatment approaches. In addition, the recent entry into force of Directive (EU) 2020/2184, concerning the quality of water intended for human consumption, has posed additional challenges for water treatment plants, with reference to the imposition of much stricter limits, especially regarding turbidity (<0.30 NTU).

To cope with the above issues and meet the more stringent regulations/standards of drinking water, ferrate(VI) (i.e., FeO_4^{2-}) has been recently proposed as one of the most broad-spectrum chemical toward several contaminants (Li et al., 2021; Marbaniang et al., 2023). Fe(VI) contains iron in its +6 oxidation state with a high reduction potential of up to 2.2 V (Luo et al., 2022a). The main advantage of Fe(VI) is that nontoxic by-products are formed after the reduction of Fe(VI). Besides, Fe(VI) reduction process provides reaction iron-intermediates which may accelerate oxidation process (Fe^{5+} and Fe^{4+}) or act as useful precipitants (Fe^{3+}), thus reducing the required dose of conventional chemicals (Zhang et al., 2021). Moreover, the possibility of producing Fe(VI) via electrochemical processes using metal scraps makes it to be considered a as a green chemical in line with circular economy approaches and potentially cheaper than conventional oxidating agents (Wang et al., 2020; Zhao et al., 2023). In the past years, several studies have been carried out using Fe(VI) for drinking water treatments. High removal performances toward manganese (Goodwill et al., 2016b), turbidity and NOM (Ma and Liu, 2002; Zhang et al., 2020) have been reported in literature using Fe(VI).

Nevertheless, several aspects remain unclear so far. First, ferrate has not been attempted for drinking water production under emergency situations related to climate change. Indeed, in previous literature the use of Fe(VI) in combination with conventional chemicals used for drinking water production is lacking. Thus, it not possible to address if increasing performance could be achieved when a drinking water treatment plant (DWTP) is subjected to worsening of the inlet water quality. Moreover, its stoichiometry, kinetics, removal mechanisms of pollutants and impact of environmental parameters (e.g., pH) are not completely clear. Specifically, the role of Fe(III) resulting from Fe(VI) reduction has not been carefully addressed. Indeed, if on the one hand it is stated that Fe(III) could potentially interact with other pollutants, on the other hand, its contribution was not quantified. In this frame, oxidation reactions with ferrate occur under conditions of excess stoichiometry, and consequently, it is not possible to assess whether the reaction products contribute to the completion of the process (Goodwill et al., 2016b). This could considerably improve pollutants removal since it could result in an in-situ simultaneous oxidation/coagulation process towards several compounds. Furthermore, the role of pH in ferrate oxidation reactions is not clear. Indeed, although some studies report high removal efficiencies of various pollutants at pH values between 4 and 9 (Tien Khoi et al., 2023; Zhang et al., 2020), in others it is stated that ferrate is stable only at pH values higher than 8.5. Consequently, this aspect requires further investigation.

Lastly, a comprehensive comparison between the performance achievable with ferrate or conventional chemicals is not available in the current literature.

Besides, in the framework of climate change, in which change of water quality could generate risk conditions for drinking water production, Fe(VI) could be exploited as an additional process to be implemented under emergency situations. In this perspective, it would be essential to evaluate its synergy with conventional reagents (e.g., coagulants/flocculants).

Considering this, the aim of this study was to comprehensively evaluate the Fe(VI) treatment to address emergency situations related to climate change, either as an alternative or in combination with conventional reagents. Specific investigations on the mechanisms for removing the main pollutants, the stoichiometry of reactions, as well as potential advantages and disadvantages, have been conducted.

2. Materials and methods

2.1 Jar test experiments

Jar test experimental procedure was used to assess the effect of Fe(VI) for removing manganese, NOM and algae. For all the experiments, jar test procedure involved a rapid mixing at 200 rpm for 1 minute followed by a slow mixing at 30 rpm for 20 minutes and finally a settled period for 60 minutes. In each of the assay, 6 batch reactors at different operating conditions (i.e., chemicals dose, pH, etc.) were studied. At the end of settling phase, a sample from the supernatant of each test was withdrawn and stored for the analyses. Each of the above pollutants was studied individually to eliminate possible interference or synergistic effects.

2.2 Manganese removal procedures

Stoichiometry of soluble manganese (Mn(II)) oxidation by potassium ferrate and permanganate was assessed by carrying out 15 experimental repetitions for each chemical. Initially, these assays were performed with high Fe(VI) dosage to allow for measurable absorbance of residual Fe(VI). Batch reactors were filled with 800 mL of deionized water (pH 7.1±0.1) to avoid having other oxidant demand except to manganese. A concentrated solution of $MnCl_2$ in deionized water was prepared and a precise volume was dosed in the batch reactors to achieve a target concentration of Mn(II). The initial Mn(II) concentration ranged between 2-14 µM (100-900 mg/L), whereas oxidants (Fe(VI) and Mn(VII)) doses were in the range 2-10 µM. The Mn(II) concentrations were based on the typical value observed in a reservoir of surface water located in Sicily (Italy) during the late summer/autumn season when influent soluble manganese concentrations usually increased up to 800-1000 µg/L. After supplying manganese chloride, Fe(VI) was added under rapid mixing conditions. In these assays, pH was measured by an ion-selective electrode probe (WTW) but not controlled. At the end of the settling phase, the residual concentrations of the Mn(II) and Fe(VI) in the filtrated water were measured to assess the moles of manganese oxidized per mole of Fe(VI) or Mn(VII) reduced.

Two additional assays, including 6 experimental trials each, were executed with Fe(VI) at pH of 9 and 7. pH was adjusted to the target values using drop-wise addition of HCl or H_2SO_4. Residual Mn(II) and Fe(VI) were measured at the end of the settling phase in the supernatant after samples filtration through 0.45 µm membrane. The same experimental approach was used to assess the removal of Mn(II) using Fe(III). Ferric chloride ($FeCl_3$) (purity 99%), was used as source of Fe(III). Fe(II) was measured to prove Mn(II) oxidation by ferric chloride via a colorimetric method.

To focus on Mn(II) oxidation kinetics with Fe(VI) and Fe(III) two assays were carried out. In a 800 mL batch reactor filled with deionized water, Mn(II) was added at the beginning of the experiment at an initial concentration of approximately 4.5 mg/L and 0.35 mg/L in the test performed with Fe(VI) and ferric chloride, respectively. Subsequently, Fe(VI) and Fe(III) were dosed. The reactors were mixed for 30 minutes with a mechanical impeller operating at rapid mixing conditions (100 rmp). Samples for Mn(II) analyses were withdrawn every 20 seconds for Fe(VI) and 4 minutes for Fe(III), then filtered through a 0.45 µm membranes to exclude particulate manganese (Mn(IV)).

2.3 Ferrate stability experiment

Stability of Fe(VI) in water solution was determined as a function of pH. The initial concentration of Fe(VI) in the solution was approximately 45 µM and the resulting pH was close to 8.4 without any addition of alkaline agent. Hereafter, the pH was stepwise decreased up to pH of 4 by adding 1 M of HCl solution. The adsorption spectra between 200-600 nm was examined by an UV-VIS spectrophotometer to measure the residual Fe(VI) concentration (510 nm) and the occurrence of Fe(III) (270 nm).

2.4 NOM and turbidity removal assays

Deionized water was artificially contaminated with NOM contained in the eluate from a mature compost sample derived from a domestic composting system fed with vegetable and pruning residues. A compost sample (1 kg) was placed in a 5 L laboratory beaker and filled with deionized water, then was mixed for 24 hours. Hereafter, the sample was left to settle for 1 h and 3 L of supernatant were collected and centrifuged at 4000 rpm for 30 minutes to remove residual particles. The supernatant was characterized in terms of total organic carbon (TOC) content and stored at 4 °C. To assess NOM removal by Fe(VI), six batch reactors were filled with deionized water and the supernatant derived from compost elution until reaching a target TOC vale of approximately 7 mg/L. Then Fe(VI) was supplied at different doses between 0-2 mgFe(VI)/L. This assay was replicated by adding a constant dose of soluble manganese (0.90 mgMn(II)/L) to assess Fe(VI) reactivity in presence of a reducing agent.

Turbidity removal assays were carried out on real water samples collected at the entrance of a drinking water treatment plant. Initial turbidity of samples was approximately 6.5 NTU and pH was close to 7.6. Jar test

procedure was carried out on 18 samples without any pH ajdustment. Specifically, in six batch reactors increasing conventional coagulant/flocculant (polyaluminum chloride - PACl) between 5-25 mg/L and a constant dose of cationic polyelectrolyte (0.10 mg/L) were dosed. The same test was replicated twice while adding a constant dose of potassium ferrate (2.5 and 4 mgFe(VI)/L). In the latter case, the pH slightly increased at about 8.1-8.3.

2.5 Algae removal

A mixture of natural algae (mostly Chlorella sp.) was used to artificially contaminate deionized water and simulate algal bloom. Two experimental assays were carried out using potassium ferrate and permanganate as oxidating agents. In each of the assays, six batch reactors were filled with deionized water and a mixture of natural algae (initial Chl-a concentration of 0.45 µg/L), then Fe(VI) and Mn(VII) were dosed at different doses (0-15 mg/L). Direct measurement of chlorophyll-a (Chl-a) in the supernatant after the settling phase was assessed to evaluate the effect of Fe(VI) and Mn(VII) on algae removal.

2.6 Chemicals

Commercial potassium ferrate (Aaron Chemical, purity 99%) was used in all the assays. Before each test, a concentrated solution of Fe(VI) was prepared by dissolving 1 g of K_2FeO_4 in 1 L of deionized water. Then, the solution was dosed in different volume to achieve the desired Fe(VI) concentration in each reactor. The concentrations of Fe(VI) in the solution and in each reactors were measured to verify the initial value. A concentrated solution of potassium permanganate ($KMnO_4$) (1.4% v/v) was used as comparison with ferrate for manganese and algae removal. Manganese chloride ($MnCl_2$) (Sigma Aldrich, purity 99%) was used as soluble manganese (Mn(II)) source for the relative assays. 1 M HCl or H_2SO_4 solutions were used to adjust pH if required by target operating conditions.

2.7 Analytical methods

Fe(VI) determinations were performed using an UV-VIS spectrophotometer by measuring the absorbance at 510 nm. A calibration line (0-10 mgFe(VI)/L) was constructed using commercial potassium ferrate (purity 99%) as a standard to measure the Fe(VI) concentration in the samples. All the samples for Fe(VI) measurement were previously filtered through 0.45 µm cellulose membrane to remove impurities. Samples for Mn(II) measurements, were filtered through 0.45 µm cellulose membrane to remove particulate manganese compounds, then analyzed with an inductively coupled plasma optical emission spectrometry (ICP OES). Total organic carbon was measured by a TOC analyser (Shimadzu). Chlorophyll-a was extracted from algae samples and measured according to the literature (Liu et al., 2011). Turbidity was measured using a portable turbidity meter (Hanna, HI93703).

3. Results and discussion

3.1 Manganese removal

3.1.1 Stoichiometry of Mn(II) oxidation by Fe(VI) and Mn(VII)

To simulate the manganese removal by ferrate under ordinary and emergency situation, Mn(II) concentration in the raw water ranged between 0.100 mg/L (ordinary situation) and 0.900 mg/L (emergency). Results for Mn(II) oxidation by potassium ferrate and permanganate are depicted in Figure 1. As pH was not controlled in both the tests, it resulted slightly different when potassium ferrate or permanganate were used. Specifically, potassium ferrate involved a slight increase of pH that ranged between 8.2-8.6, showing an increasing trend with the Fe(VI) dose in accordance with previous study (Lim and Kim, 2009). In contrast, pH slightly decreased from 7.6 to 7.2 when the potassium permanganate dose was increased.

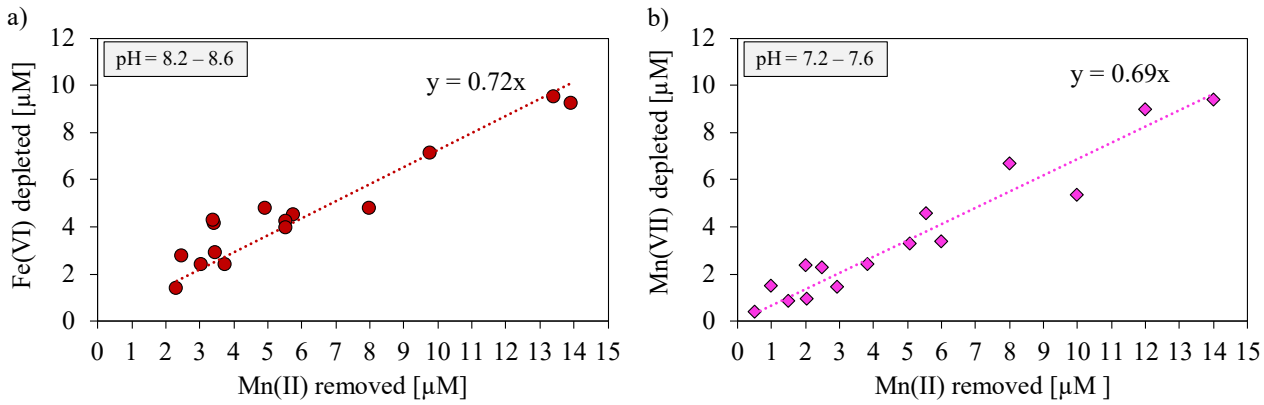

Figure 1: Relationship between the Fe(VI) (a) and Mn(VII) (b) depleted and the Mn(II) oxidized.

Linear regression of Fe(VI) and Mn(VII) depleted with Mn(II) removed resulted very similar, showing a slope of 0.72 and 0.69 for Fe(VI) and Mn(VII), respectively. In both the cases, the y-intercept was set to zero in order to consider no Mn(II) oxidation at zero oxidant dose. The above results indicated that the overall molar stoichiometry of the Mn(II) oxidation by Fe(VI) and Mn(VII) without any other oxidant demand was approximately 2:3 according to the following global reactions:

$$2\,K_2FeO_4 + 3\,MnCl_2 + 2\,H_2O \rightarrow 3\,MnO_2 + 2\,FeCl_3 + 4\,KOH \quad (1)$$

$$2\,KMnO_4 + 3\,MnCl_2 + 2\,H_2O \rightarrow 5\,MnO_2 + 2\,KCl + 4\,HCl \quad (2)$$

The above reactions indicated that the Mn(II) removal mechanisms exerted by Fe(VI) and Mn(VII) involved the transfer of two electrons to Mn(II) that formed manganese dioxide (Mn(IV)-Pyrolusite) in insoluble form precipitated at the end of settling phase.

Considering Eq.1, it should be noted that at the end of the reaction, Fe(VI) was reduced to Fe(III), which might react as coagulant-flocculant agent, thus providing additional removal capacity toward other pollutants. Nevertheless, any contribution of Fe(III) to Mn(II) removal was observed in these assays. The production of hydroxyl group (potassium hydroxide) was in line with the pH increase observed during the batch assays. In contrast, Mn(VII) was reduced to Mn(IV) thus contributing to the increase of manganese dioxide in the sludge (+40% than Fe(VI)), as reported in previous literature (Gregory and Carlson, 2003; Tobiason et al., 2016). From a management point of view, special attention should be paid on this aspect, especially when flocculation and clarification is performed in sludge blanket units (Fouad and Hassan, 2018). Indeed, if sludge blanket is retained for a long period, eventually occurrence of reducing conditions within the sludge bed could led to transformation of Mn(IV) to Mn(II) and its release in the effluent. Therefore, since the amount of manganese dioxide produced is approximately 40% lower when using potassium ferrate, the latter utilization in place of potassium permanganate could contribute to reduce the risk of Mn(II) release from sludge.

Overall, the stoichiometry of Mn(II) oxidation by Fe(VI) observed in this study was very similar to what reported in previous literature (Goodwill et al., 2016c). Specifically, these authors observed that the overall molar stoichiometry between Fe(VI) and Mn(II) was 0.67 under similar operating conditions of the present study (absence of other oxidant demand). In contrast with what reported in the above study, in the present work pH was slightly higher (8.2-8.6 vs 6.5-7.5), thus indicating that at higher pH the stoichiometry of the Mn(II) oxidation reaction did not change significantly.

Other studies referred that Fe(VI) reduction resulted to intermediates like Fe(V) and Fe(IV) having higher reactivity than Fe(VI) that could reacted with Mn(II) (Sharma et al., 2022; Zhao et al., 2023). However, the Fe(VI) intermediates were not measured in this study and their presence was only hypothesized. Nevertheless, as reported in previous literature (Goodwill et al., 2016a), if Fe(V) and Fe(IV) were formed as intermediates in the reaction and they did not oxidize Mn(II), the slope of Fe(VI)/Mn(II) would result higher as more Fe(VI) would be necessary for Mn(II) oxidation.

To assess the effect of pH on the stoichiometry of Mn(II) oxidation by Fe(VI), two additional assays were carried out at pH 7 and 9. The results are reported in Figure 2.

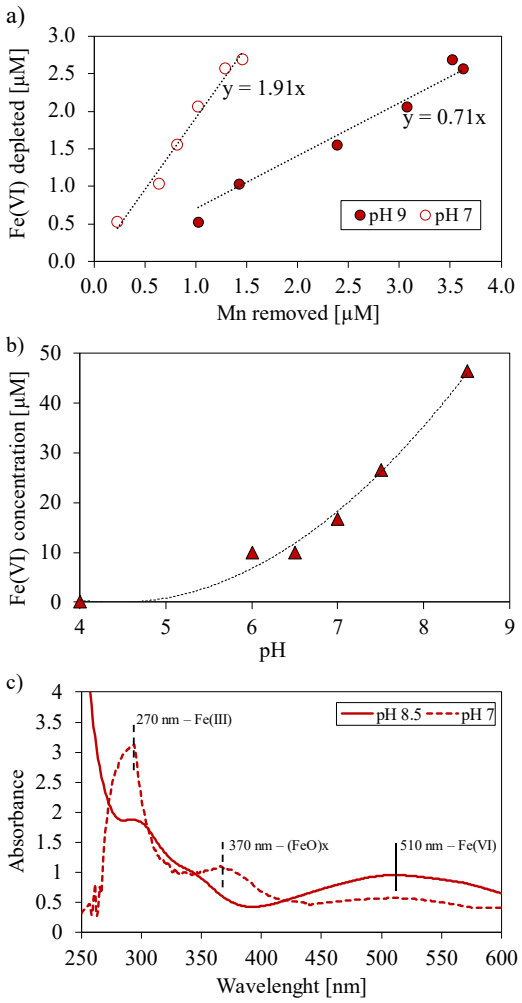

Figure 2: Relationship between the Fe(VI) and Mn(II) oxidized at pH 7 and 9 (a); Fe(VI) concentration in a Fe(VI) solution (10 mg/L in deionized water) under different pH (b); UV-vis absorption spectrum of the Fe(VI) solution at different pH (c).

The assay performed at pH 9 reproduced similar results of the previous, in which the overall molar stoichiometry between Fe(VI) and Mn(II) was approximately 0.70, thus providing results reliability (Fig. 2a). Nevertheless, in contrast to what observed by Goodwill and coauthors (Goodwill et al., 2016c), in this study the stoichiometry of Mn(II) oxidation reaction by Fe(VI) at pH close to neutral was significantly different. Specifically, the slope of Fe(VI)/Mn(II) resulted approximatively 1.90, thus three times higher than that observed in the previous study (0.67). This result suggested that at lower pH, Mn(II) oxidation was performed by other reaction intermediates as more Fe(VI) was required for Mn(II) oxidation than the stoichiometric value (0.67). This suggested that at pH close to neutral, ferrate destabilization occurred and Mn(II) oxidation was obtained by other iron ions having a lower oxidation potential. To better understand this, additional measurement of Fe(VI) stability in deionized water without oxidant demand were performed. The results reported in Fig. 2b revealed that the amount of Fe(VI) significantly reduced when the pH of the solution was decreased to neutral value. In more detail, Fe(VI) concentration decreased proportionally with pH reduction and when pH was decreased from 9 to 7, the residual Fe(VI) concentration dropped of more than 65%, while Fe(III) was formed simultaneously. Indeed, as can be observed in Fig. 2c, at pH of 7 the peak of absorbance at 510 nm which identified Fe(VI) was significantly lower than pH 9. Besides, at pH of 7 other peaks were clearly observed at 270 nm and 370 nm that identified the occurrence of Fe(III) and unspecified iron oxide, respectively (Behera et al., 2012).

In contrast to what reported in previous studies, ferrate was not observed at pH lower than 6 (Zhang et al., 2020). In a recent study, it was demonstrated that Fe(VI) decay was faster at pH lower than 9 and its complete disappearance occurred at pH < 6.0 (Wang et al., 2022). The same authors observed that Fe(V) and Fe(IV) started to generated from Fe(VI) decay at pH lower than 8. The above results indicated that when Mn(II) oxidation by Fe(VI) was carried out at pH lower than 9, the oxidative effect of Fe(VI) noticeably decreased,

whereas in contrast the contribution of other intermediated likely increased. In this sense, other studies focusing on the role of Fe(V) and Fe(IV) on Mn(II) oxidation mechanisms should be necessary.

3.1.2 Effect of Fe(III) on Mn(II) removal

Batch assays performed with potassium ferrate solution at neutral pH revealed that Fe(III) was the main iron compound derived from Fe(VI) decay/reduction. Basen on the literature review, any studies reported the possible role of Fe(III) in Mn(II) removal. To assess this, a specific assay in deionized water without oxidant demand (except of manganese) was performed. In this case, the initial Mn(II) concentration ranged between 2-14 µM, whereas Fe(III) dose was in the range 5-25 µM. Figure 3 shows the results for Mn(II) removal by Fe(III).

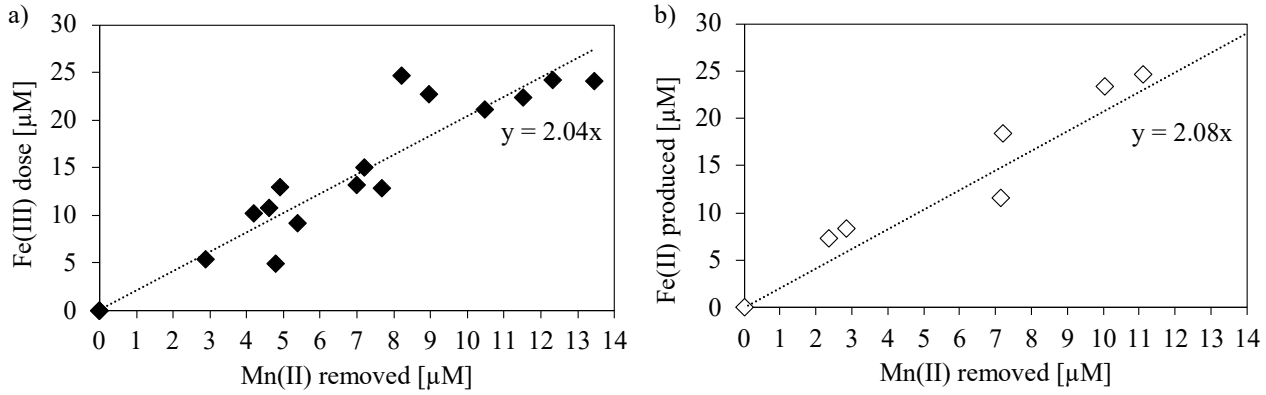

Figure 3: Linear regression between Fe(III) dose and Mn(II) removed (a); relationship between Fe(II) produced during Fe(III)-Mn(II) reaction and Mn(II) depleted (b).

The linear regression of the data indicated that the molar stoichiometry of the reaction between Fe(III) and Mn(II) was approximately 2:1. This value was similar to that achieved in the assay performed with potassium ferrate at neutral pH (1.90), thus suggesting that in that case the removal of Mn(II) was mainly attributable to Fe(III). It was interesting to note that at the end of the assay an increasing concentration of Fe(II) was observed, which resulted proportional to Mn(II) removed. This result indicated that Fe(III) underwent one electron transfer to Fe(II) and Mn(II) was oxidized to Mn(IV) as consequence. Based on the above results, the stoichiometry of Mn(II) removal by Fe(III) was hypothesized:

$$2\,FeCl_3 + MnCl_2 + 2\,H_2O \rightarrow MnO_2 + 2\,FeCl_2 + 4\,HCl \quad (3)$$

The implication of the above equation is that theoretically the oxidation reaction of Mn(II) by Fe(VI), as shown in Equation 1, could further proceed because the Fe(III) produced as a result of the reaction would be capable of further oxidizing Mn(II), although at a higher stoichiometric ratio compared to Fe(VI). However, in the assays carried out with Fe(VI), no contribution of Fe(III) to the overall oxidation reaction of Mn(II) was observed. In fact, if this had occurred, the demand for Fe(VI) in the oxidation of Mn(II) would have been lower, and the stoichiometric ratio would have been lower than 0.70. One possible explanation for this result could be attributed to the fact that the Mn oxidation assays with Fe(VI) were carried out with an excess of the latter. Indeed, as reported by Goodwill and co-authors (Goodwill et al., 2016b), the theoretical Fe(VI)/Mn(II) stoichiometric ratio is 0.67. Consequently, the presence of excess Fe(VI) implied that Mn(II) was preferentially oxidized by Fe(VI) rather than Fe(III), both due to the higher reactivity of the Fe(VI) molecule and its higher concentration in the solution.

3.1.3 Kinetics of Mn(II) oxidation by Fe(VI) and Fe(III)

To provide more insight into the Mn(II) oxidation reaction by Fe(VI) and the possible role of its reaction intermediates on the process, additional batch assays were carried out to investigate on manganese oxidation kinetics. Figure 4 depicts the results of equation 1 and equation 3 kinetics.

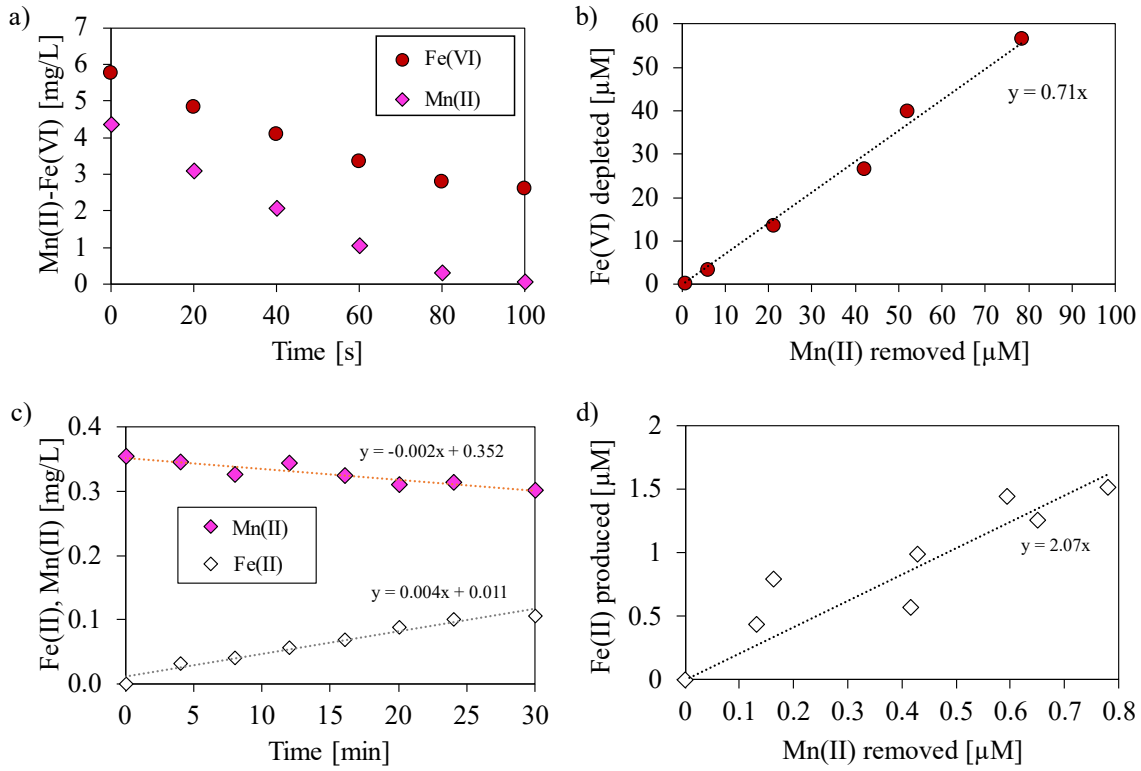

Figure 4: Kinetic of Mn(II) oxidation with Fe(VI) (a); relationship between Fe(VI) depleted and Mn(II) oxidized during the kinetic assay with Fe(VI) (b); Kinetic of Mn(II) oxidation with Fe(III) (c); relationship between Fe(II) produced and Mn(II) oxidized during the kinetic assay with ferric chloride (d)

The oxidation reaction of Mn(II) by Fe(VI) exhibited a zero-order kinetic up to a concentration of approximately 0.30 mgMn(II)/L (Fig. 4a). The Mn(II) oxidation rate resulted approximately 9.97×10^{-4} mM/s. At the end of the reaction, residual Fe(VI) was still measurable, indicating that the oxidation reaction of Mn(II) to Mn(IV) was entirely attributed to Fe(VI). To confirm this, the stoichiometric ratio between consumed Fe(VI) and removed Mn(II) showed a linear regression with a slope of approximately 0.70, consistent with previous results and with the theoretical molar ratio between Fe(VI) and Mn(II) of 2:3 (Fig. 4b). The formation of Fe(II) was not observed at the end of this reaction, confirming that the produced Fe(III) did not react further.
The oxidation of Mn(II) by Fe(III) exhibited a zero-order kinetics similar to Fe(VI) but much slower (Fig. 4c). In fact, the removal rate of Mn(II) by Fe(III) was found to be 5.5×10^{-7} mM/s, thus three orders of magnitude lower than that of Fe(VI). The simultaneous production of Fe(II) in a molar ratio with Mn(II) of approximately 2 indicated that the reaction proceeded according to Equation 3 (Fig. 4d).
The aforementioned results confirmed the hypothesis regarding the contribution of Fe(VI) and Fe(III) to the oxidation of Mn(II). Since the oxidation reaction of Mn(II) with Fe(VI) is kinetically much faster than with Fe(III), in the presence of residual Fe(VI), it would rapidly oxidize the remaining Mn(II) compared to Fe(III). Consequently, although Fe(III) potentially produced from the reduction of Fe(VI) could remove Mn(II), this reaction cannot be observed when residual Fe(VI) is available because Mn(II) would be preferentially oxidized by Fe(VI).

3.1.4 Overall reaction of Mn(II) removal by Fe(VI)

Based on the results obtained from the kinetics of the oxidation reactions of Mn(II) with Fe(VI) and Fe(III), it has been observed that the reaction involving Fe(III) could be concurrent with that of Fe(VI). Consequently, this reaction can only occur if Fe(VI) is entirely depleted, i.e., if it is dosed at a stoichiometric deficit compared to Mn(II). From a theoretical standpoint, the resulting overall reaction from Equations 1 and 3 would be as follows (Equation 4):

$$2\,K_2FeO_4 + 4\,MnCl_2 + 2\,H_2O \rightarrow 4\,MnO_2 + 2\,FeCl_2 + 4\,KCl \qquad (4)$$

To verify this hypothesis, further oxidation assays of Mn(II) with Fe(VI) were carried out, with different Fe(VI) dosages within the range of 0-14 µM. The results are shown in Figure 5.

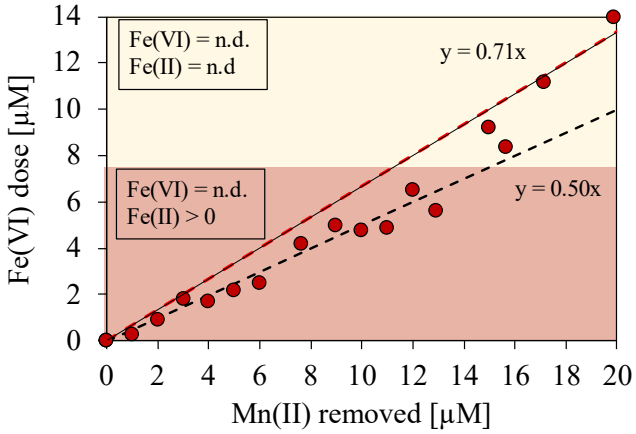

Figure 5: Relationship between the Fe(VI) dose and the Mn(II) removed

At low dosages of Fe(VI), the amount of removed Mn(II) was higher than the theoretical value predicted by Equation 1. Specifically, for Fe(VI) dosages below 8 µM, no residual Fe(VI) was detected, and the presence of Fe(II) was observed. In these tests, the average molar ratio between utilized Fe(VI) and removed Mn(II) was approximately 0.55, and the simultaneous presence of Fe(II) suggested that the Fe(III) produced from the reduction of Fe(VI) contributed to further oxidizing Mn(II). At Fe(VI) dosages greater than 8 µM, the average molar ratio between removed Fe(VI) and oxidized Mn(II) was approximately 0.71. In this case as well, no residual Fe(VI) was measured, but at the same time, no formation of Fe(II) was observed, suggesting that the formed Fe(III) did not react since all the available Mn(II) had already been oxidized by Fe(VI).
Therefore, in contrast to what reported in previous studies (Goodwill et al., 2016b), Fe(III) could contribute to remove Mn(II) from water, resulting in a decrease of the stoichiometric ratio between Fe(VI) and Mn(II).
In conclusion, it can be stated that the involvement of Fe(III) in the oxidation reaction of Mn(II) starting from Fe(VI) requires a slight deficit dosage of Fe(VI). However, considering the low reactivity of Fe(III) and the slow oxidation kinetics it is reasonable to assess that this process might not occur adequately within the pre-oxidation units of drinking water treatment plants due to the low hydraulic residence times. Nevertheless, Fe(III) could be effectively useful for metals and colloids removal, given its tendency to form hydroxides (Siéliéchi et al., 2008; Wu et al., 2010).
Overall, even not considering the contribution of Fe(III) to manganese oxidation, the dosage of K_2FeO_4 necessary was approximately 2.40 mg K_2FeO_4 per mg of Mn(II). Compared to other oxidants used for Mn(II) oxidation, the dose of Fe(VI) required was very similar. Indeed, in the absence of other oxidant demands chlorine dioxide oxidation of Mn(II) follows a stoichiometry of 2.45 mgClO_2 per mg of Mn(II), permanganate (MnO_4^-) required approximately 1.95 mg$KMnO_4$ per mg of Mn(II), whereas ozone (O_3) oxidizes Mn(II) with a lower demand of 0.87 mgO_3 to 1.0 mgMn(II) ratio although incurring very high production costs (Tobiason et al., 2016). Besides, while those oxidants can led to downstream water quality problems like in situ formation of permanganate (ozone), formation of by-product chlorite (chlorine dioxide) or formation of additional particulate Mn(IV) that must be removed (permanganate), Fe(VI) by-products are not harmful and potentially useful to the water treatment process (Zhang et al., 2020).

3.2 Removal of NOM and turbidity

3.2.1 Removal of NOM with ferrate and permanganate

Removal of NOM by Fe(VI) was studied to focus on the degradation capacity of Fe(VI) toward organic pollution in drinking water. Figure 6 shows the trends of residual TOC as the dosage of Fe(VI) increases, with or without soluble manganese as Fe(VI) activator. Results were compared with potassium permanganate as conventional oxidant.

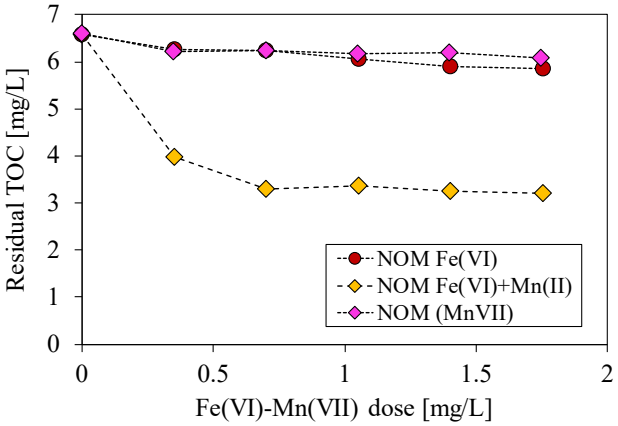

Figure 6: Trend of residual TOC at increasing dose of permanganate and ferrate with or without Mn(II) in the solution (pH = 8).

In the presence of NOM only in the water, the TOC removal efficiency was found to be very modest, and results were comparable with those obtained with Mn(VII). In fact, at the maximum Fe(VI) dosage of approximately 1.8 mg/L, removed TOC was only 10%, indicating a poor oxidative capacity of Fe(VI) under alkaline condition (pH = 8). These findings aligned with observations reported in other studies regarding the transformation and removal of NOM using Fe(VI) (Zhang et al., 2020). According to previous literature, at an alkaline condition the reduction potential of Fe(VI) is lower than at pH lower than 7, thus leading to poor NOM mineralization capacity (Lim and Kim, 2009; Zhang et al., 2020). In this context, Deng and co-authors suggested that NOM removal by ferrate increased as ferrate decomposition was improved (Deng et al., 2018). Therefore, as at high pH Fe(VI) is stable in its form, poor NOM removal was observed. In a recent study, it was observed that the single use of ferrate for NOM removal was effective at pH of 5, thus suggesting that the more reactive forms towards NOM removal derived from Fe(VI) decomposition (Tien Khoi et al., 2023).
When soluble manganese was also added to the medium (Mn(II) = 0.9 mg/L), the TOC removal efficiency increased significantly, reaching around 55%. In this case, in fact, although at low dose of Fe(VI) (0.7 mg/L), the residual TOC was 3.3 mg/L; furthermore, as the Fe(VI) dose increased, the residual TOC remained nearly constant, thus suggesting that the maximum removal was already achieved at the lower doses. Previous studies demonstrated that the oxidation capacity of Fe(VI) depends on the involvement of intermediate iron species resulting from Fe(VI) reduction (Barışçı, 2017). In more detail, it has been demonstrated that generation of Fe(V) and Fe(IV) as intermediate of Fe(VI) reduction to Fe(III) is a crucial step for achieving high oxidation performances toward organic matter (Luo et al., 2022a, 2022b). Indeed, such molecules are reported to have up to 2-5 order of magnitude more reactive than Fe(VI) (Sun et al., 2019). In this sense, a recent study demonstrated that colloids manganese dioxide were able to accelerate the formation of Fe(V) and Fe(IV) from Fe(VI), leading to the formation of reactive intermediates very active toward NOM (Luo et al., 2022b). In this case, Mn(II) oxidation to Mn(IV) could likely contributed to activate Fe(VI) and promoted NOM removal. Nevertheless, it should be stressed that the absence of Mn or its concentration being insufficient to generate significant concentrations of Fe(VI) reduction intermediates could result in an ineffective reduction of organic substances in water. However, it should be noted that literature reports various compounds capable of serving as Fe(VI) activators, many of which are naturally present in river or reservoir waters (Sharma et al., 2022).
Moreover, it should be considered that when ferrate decomposition occur, Fe(III) is generated. In other literature studies, it was reported that ferrate pre-oxidation had positive effect on coagulation/flocculation of NOM (Jiang et al., 2016) because of Fe(III) production. Indeed, negatively charged compound of NOM are removed by iron ions by formation of colloidal hydroxides (Liao et al., 2017). Therefore, the simultaneous generation of Fe(III) deriving from Fe(VI) reduction is of significant importance as it may allow the removal of NOM from water and at the same time the use of lower coagulant doses due to the Fe(III) introduced by ferrate decomposition.

3.2.1 Removal of turbidity: using ferrate as enhancer coagulant/flocculant

Results on turbidity removal using conventional coagulant/flocculant and Fe(VI) as enhancer agent are presented in Figure 7. As the dose of PACl increased, the residual turbidity sharply decreased below 1 NTU

and a minimum of 0.41 NTU was achieved at 20mgPACl/L dose. At higher dose, the residual turbidity increased, thus suggested that the excess of PACl caused by itself an increase of turbidity. Although very high removal of turbidity was obtained (93%), the lowest value obtained resulted higher than the limit introduced by the new Directive (EU) 2020/2184 already in force in many member states.

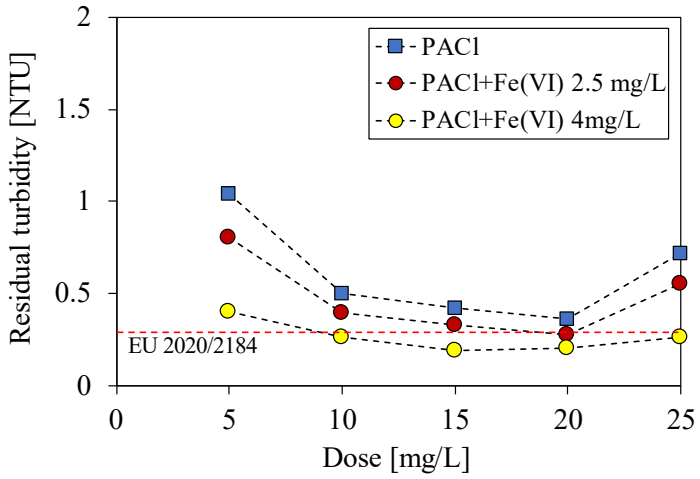

Figure 7: Residual turbidity of real surface water samples at different dose of PACl without (■) or with Fe(VI) at 2.5 mg/L (●) and 4 mg/L (●). The red dotted line indicates the limit imposed by Directive EU 2020/2184.

Addition of a constant dose of Fe(VI) (2.5mg/L) improved turbidity removal. Indeed, while dosing Fe(VI) a residual turbidity lower than 0.30 NTU (0.27 NTU) was obtained at 20 mgPACl/L. Therefore, compliance with the regulatory limit and approximately 25% of conventional chemicals saving was achieved using Fe(VI) as coagulant/flocculant enhancer. Nevertheless, a further increase of Fe(VI) dose to 4 mg/L significantly decreased the residual turbidity. A minimum of 0.19 NTU was obtained at a PACl dose of 15 mg/L, whereas the value of residual turbidity closer to the regulation limit (0.27 NTU) was achieved at 10 mgPACl/L. Overall, the obtained result were in line with previous studies, in which high turbidity removal (>80%) from reservoir water was achieved using Fe(VI) only (Zhang et al., 2020). Nevertheless, in that study, the residual turbidity using Fe(VI) only never resulted lower than 2 NTU, indicating that Fe(VI) should be used as a complementary treatment to conventional processes. The present study demonstrated that the addition of Fe(VI) to conventional coagulant/flocculant agent allowed a noticeable decrease of PACl dose (> 50%) to comply 0.30 NTU. A significantly smaller dose of PACl can significantly reduce the chemical requirements, providing the potential for significant cost savings in the treatment of drinking water. It is important to emphasize that Fe(VI) is used as an oxidant rather than a pure coagulant/flocculant agent. Hence, the operating cost associated with Fe(VI) use should not be considered an additional expense for the coagulation/flocculation process. As previously mentioned, the byproducts of Fe(VI) oxidation, such as ferric ion or ferric hydroxide, act as fundamental coagulant resources. (Jiang et al., 2018). Therefore, Fe(VI) can also perform coagulation after degrading organic matter and microorganisms or oxidizing inorganic substances (e.g., metals). Based on the achieved results, it can be stated that Fe(VI) allow complying more stringent regulations and at the same time providing additional removal capacity of turbidity and treatment robustness in the case that extreme event entailed increases in raw water turbidity.

3.3 Algae removal

3.3.1 Performance and mechanisms of algae removal

Potassium ferrate was tested to remove algae and its efficiency was compared with another oxidating agent (i.e., potassium permanganate). Figure 8 reports the results of the assays carried out with the above reagents (Fig. 8a), the removal efficiency achieved (Fig. 8b) and the removal mechanisms hypothesized (Fig. 8c).

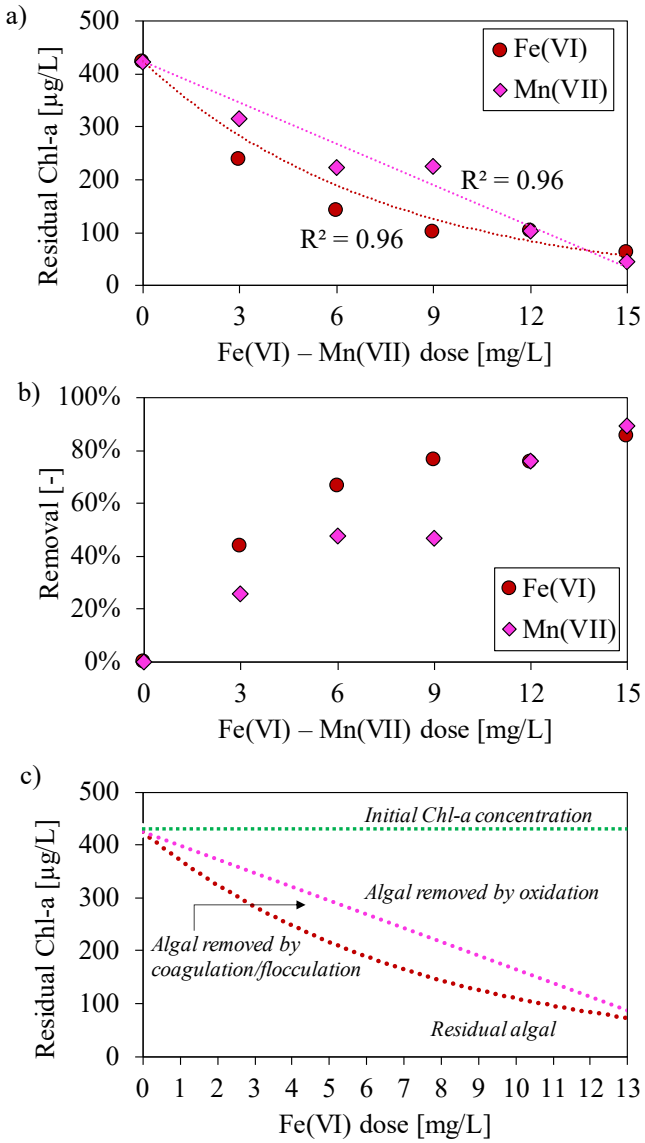

Figure 8: Removal of Chl-a with Fe(VI) and Mn(VII) at different dose (a); removal efficiency of Chl-a with increasing dosage of Fe(VI) and Mn(VII) (b); possible mechanisms of algal removal by ferrate and permanganate (c).

The concentration of Chl-a measured in the supernatant at the end of the jar test procedure gradually decreased with increasing doses of both Fe(VI) and Mn(VII) (Fig. 8a). Specifically, the lowest Chl-a concentration of approximately 80 µg/L was achieved at the maximum dosage for both reagents (15 mg/L). However, it should be noted that the trend of Chl-a concentration removal with Fe(VI) was different from that of Mn(VII). While a nearly linear relationship was observed between the dosage of Mn(VII) and Chl-a removal (Chen and Yeh, 2005), the regression line for Fe(VI) followed a decreasing exponential trend. This implied that at the same reagent dosage, the residual Chl-a concentration was lower with Fe(VI) compared to that obtained with Mn(VII). However, this difference gradually diminished with increasing reagent doses, and at the maximum dosage, both reagents provided the same 90% removal efficiency (Fig. 8b). Nevertheless, Fe(VI) allowed for removal efficiencies of around 80% even at lower dosages, approximately 30% lower than Mn(VII).

The exponential trend observed in the curve interpolating the data in Figure 7a indicated that besides Fe(VI), there were other compounds involved in the algae removal reaction, and their contribution decreased as the dosage of Fe(VI) increased. In previous study, it was stated that several process mechanisms are thought to be responsible for the efficient removal of algae through pre-oxidation with potassium ferrate (Kubiňáková et al., 2017). Specifically, the inactivation of algae and the subsequent formation of an intermediate form of iron, induced by Fe(VI) pre-oxidation, acted as a coagulant aid, ultimately resulting in the formation of algae

agglomerates (Ma and Liu, 2002). Based on the obtained results, it was hypothesized that the Fe(III) generated from the reduction of Fe(VI) actively contributed to algae removal, albeit through a different mechanism than observed for manganese removal. In fact, the presence of Fe(II) was not detected in any of the analyzed samples, indicating that the effect of Fe(III) on algae was not primarily oxidative but rather coagulation/flocculation (Fig. 8c). As observed for manganese removal, it is possible that at low Fe(VI) dosages, being stoichiometrically deficient compared to the target pollutant (algae in this case), it may be depleted before complete removal of the pollutant. Consequently, slower concurrent reactions involving the oxidation byproducts (i.e., Fe(III)), can occur and contribute to reduce the residual algae concentration. On the other hand, at high Fe(VI) concentrations, the increased availability of Fe(VI) led to algae removal primarily through oxidation and mineralization mechanisms.
However, it should be noted that compared to conventional oxidizing agents, Fe(VI) allows for a significant improvement in algae removal efficiencies at lower dosages, while reducing the risk of potentially harmful byproduct formation.

3.3.2 Integration of ferrate with conventional flocculating agent for algal removal

The removal effect of algae by Fe(VI) was also evaluated synergistically with conventional coagulant/flocculant agents used in drinking water treatment plants. Figure 9 shows the trend of residual Chl-a concentration as a function of increasing coagulant dosage (PACl) without and with a constant dosage of Fe(VI) and Mn(VII). In particular, the results of the two assays with constant Fe(VI) and Mn(VII) concentrations shown in Figure 8 refer to the optimal dosage of ferrate (Fig. 9a), which was 9 mg/L (as Fe(VI)), and permanganate dosage (Fig. 9b) of 15 mg/L (as Mn(VII)), in accordance with the previous test.

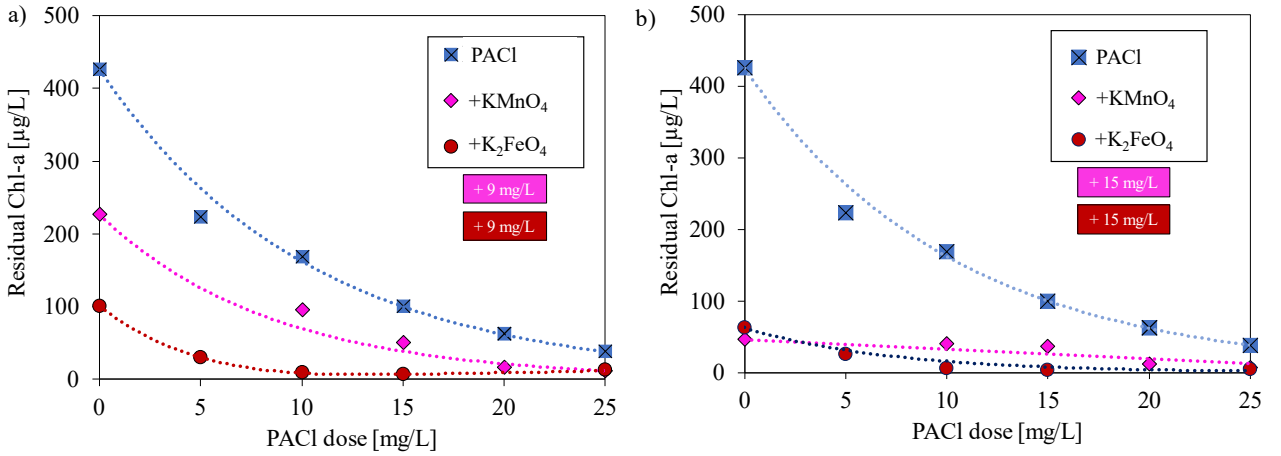

Figure 9: Chl-a removal using PACl at different dosage with the addition of 9 mg/L of Mn(VII) and Fe(VI) (a) and 15 mg/L of Mn(VII) and Fe(VI).

PACl was capable of effectively removing algae, although at a high consumption (> 25 mgPACl/L). Certainly, the dosage of potassium permanganate on one hand and Fe(VI) on the other hand allowed for a reduction in the required flocculant quantity. Specifically, to achieve Chl-a concentrations on the order of 10 mg/L, approximately 20 mg/L of PACl had to be dosed in addition to 15 mg/L of potassium permanganate (as Mn(VII)), while for Fe(VI), the PACl dosage was approximately half (10 mg/L) and the Fe(VI) dosage was 9 mg/L. The above results were in line with previous studies in which a removal of algae close to 90% was achieved by supplying 5 mg/L of Fe(VI) with a 15 mg/L of alumn (Ma and Liu, 2002).
The use of Fe(VI) reduces the conventional coagulant dosage by almost 50% to lower the algae concentration. This result is important, especially in a context where the risk of algal blooms is very high due to climate change, and the frequency of such phenomena is more frequent. Consequently, Fe(VI) can be used as a reagent under normal conditions as well as in emergency situations, considering the possibility of on-site production when needed through electrochemical methods.

Conclusions

In the present study, the potential of Fe(VI) in removing three classes of pollutants (manganese, NOM, algae) was tested. The presence of these pollutants in surface waters intended for human consumption increased in

recent years because of climate change, thus creating emergency situations to be faced. The obtained results confirmed that Fe(VI) can achieve high removal efficiencies for all the examined contaminants, often outperforming conventionally used reagents. Specifically, for manganese removal, the Fe(VI) dose can be lower than the stoichiometric dose (< 2 mol of Fe(VI) per 3 mol of Mn(II)), as the reaction by-products (Fe(III)) can contribute to further Mn(II) removal. Activation of Fe(VI) is required for NOM removal, which can be achieved through the simultaneous presence of soluble manganese in the water. Furthermore, the use of Fe(VI) allows for a reduction of approximately 50% in the quantity of oxidizing/coagulating agents required for algae and turbidity removal. Therefore, treating drinking water with Fe(VI) represents a promising process that can be used as an alternative or in conjunction with conventional methods to address the challenges posed by climate change, ensuring high quality standards and process sustainability.

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References

Aiken, M.L., Pace, C.E., Ramachandran, M., Schwabe, K.A., Ajami, H., Link, B.G., Ying, S.C., 2023. Disparities in Drinking Water Manganese Concentrations in Domestic Wells and Community Water Systems in the Central Valley, CA, USA. Environ. Sci. Technol. 57, 1987–1996. https://doi.org/10.1021/acs.est.2c08548

Barışçı, S., 2017. The disinfection and natural organic matter removal performance of electro-synthesized ferrate (VI). J. Water Process Eng. 20, 84–89. https://doi.org/10.1016/j.jwpe.2017.10.005

Behera, S.S., Patra, J.K., Pramanik, K., Panda, N., Thatoi, H., 2012. Characterization and Evaluation of Antibacterial Activities of Chemically Synthesized Iron Oxide Nanoparticles. World J. Nano Sci. Eng. 02, 196–200. https://doi.org/10.4236/wjnse.2012.24026

Calero Preciado, C., Boxall, J., Soria-Carrasco, V., Martínez, S., Douterelo, I., 2021. Implications of Climate Change: How Does Increased Water Temperature Influence Biofilm and Water Quality of Chlorinated Drinking Water Distribution Systems? Front. Microbiol. 12, 1–15. https://doi.org/10.3389/fmicb.2021.658927

Chen, J.J., Yeh, H.H., 2005. The mechanisms of potassium permanganate on algae removal. Water Res. 39, 4420–4428. https://doi.org/10.1016/j.watres.2005.08.032

Dao, P.U., Heuzard, A.G., Le, T.X.H., Zhao, J., Yin, R., Shang, C., Fan, C., 2024. The impacts of climate change on groundwater quality: A review. Sci. Total Environ. 912, 169241. https://doi.org/10.1016/j.scitotenv.2023.169241

Deng, Y., Jung, C., Liang, Y., Goodey, N., Waite, T.D., 2018. Ferrate(VI) decomposition in water in the absence and presence of natural organic matter (NOM). Chem. Eng. J. 334, 2335–2342. https://doi.org/10.1016/j.cej.2017.12.006

DeSimone, L.A., Ransom, K.M., 2021. Manganese in the Northern Atlantic Coastal Plain aquifer system, eastern USA—Modeling regional occurrence with pH, redox, and machine learning. J. Hydrol. Reg. Stud. 37, 100925. https://doi.org/10.1016/j.ejrh.2021.100925

Fouad, M., Hassan, S., 2018. The performance of sludge blanket clarifier against conventional settler under high water turbidity conditions. Water Pract. Technol. 13, 642–653. https://doi.org/10.2166/WPT.2018.079

Freeman, O., Ovie, O., Omoregie, I., 2017. Effect of Climate Change through Temperature Increase on Heavy Metals Concentrations in Water and Sediment of Ekpan Creek, Delta State, Nigeria. Adv. Res. 10, 1–16. https://doi.org/10.9734/air/2017/34754

Gobler, C.J., 2020. Climate Change and Harmful Algal Blooms: Insights and perspective. Harmful Algae 91, 101731. https://doi.org/10.1016/j.hal.2019.101731

Goodwill, J.E., Jiang, Y., Reckhow, D.A., Tobiason, J.E., 2016a. Laboratory assessment of ferrate for drinking

water treatment. J. Am. Water Works Assoc. 108, E164–E174. https://doi.org/10.5942/jawwa.2016.108.0029
Goodwill, J.E., Mai, X., Jiang, Y., Reckhow, D.A., Tobiason, J.E., 2016b. Oxidation of manganese(II) with ferrate: Stoichiometry, kinetics, products and impact of organic carbon. Chemosphere 159, 457–464. https://doi.org/10.1016/j.chemosphere.2016.06.014
Goodwill, J.E., Mai, X., Jiang, Y., Reckhow, D.A., Tobiason, J.E., 2016c. Oxidation of manganese(II) with ferrate: Stoichiometry, kinetics, products and impact of organic carbon. Chemosphere 159, 457–464. https://doi.org/10.1016/j.chemosphere.2016.06.014
Graham, D.J., Bierkens, M.F.P., van Vliet, M.T.H., 2024. Impacts of droughts and heatwaves on river water quality worldwide. J. Hydrol. 629, 130590. https://doi.org/10.1016/j.jhydrol.2023.130590
Graham, N.J.D., Khoi, T.T., Jiang, J.Q., 2010. Oxidation and coagulation of humic substances by potassium ferrate. Water Sci. Technol. 62, 929–936. https://doi.org/10.2166/wst.2010.369
Gregory, D., Carlson, K., 2003. Effect of soluble Mn concentration on oxidation kinetics. J. / Am. Water Work. Assoc. 95, 98–108. https://doi.org/10.1002/j.1551-8833.2003.tb10273.x
Hashempour, Y., Nasseri, M., Mohseni-Bandpei, A., Motesaddi, S., Eslamizadeh, M., 2020. Assessing vulnerability to climate change for total organic carbon in a system of drinking water supply. Sustain. Cities Soc. 53, 101904. https://doi.org/10.1016/j.scs.2019.101904
Hung, M.T., Liu, J.C., 2006. Microfiltration for separation of green algae from water. Colloids Surfaces B Biointerfaces 51, 157–164. https://doi.org/10.1016/j.colsurfb.2006.07.003
Jarsjö, J., Andersson-Sköld, Y., Fröberg, M., Pietroń, J., Borgström, R., Löv, Å., Kleja, D.B., 2020. Projecting impacts of climate change on metal mobilization at contaminated sites: Controls by the groundwater level. Sci. Total Environ. 712. https://doi.org/10.1016/j.scitotenv.2019.135560
Jiang, J.-Q., Stanford, C., Petri, M., 2018. Practical application of ferrate(VI) for water and wastewater treatment – Site study's approach. Water-Energy Nexus 1, 42–46. https://doi.org/10.1016/j.wen.2018.05.001
Jiang, Y., Goodwill, J.E., Tobiason, J.E., Reckhow, D.A., 2016. Impacts of ferrate oxidation on natural organic matter and disinfection byproduct precursors. Water Res. 96, 114–125. https://doi.org/10.1016/j.watres.2016.03.052
Kubiňáková, E., Híveš, J., Gál, M., Fašková, A., 2017. Effect of ferrate on green algae removal. Environ. Sci. Pollut. Res. 24, 21894–21901. https://doi.org/10.1007/s11356-017-9846-z
Leveque, B., Burnet, J.B., Dorner, S., Bichai, F., 2021. Impact of climate change on the vulnerability of drinking water intakes in a northern region. Sustain. Cities Soc. 66, 102656. https://doi.org/10.1016/j.scs.2020.102656
Li, B., Guo, R., Tian, J., Wang, Z., Qu, R., 2021. New Findings of Ferrate(VI) Oxidation Mechanism from Its Degradation of Alkene Imidazole Ionic Liquids. Environ. Sci. Technol. 55, 11733–11744. https://doi.org/10.1021/acs.est.1c03348
Liao, P., Li, W., Jiang, Y., Wu, J., Yuan, S., Fortner, J.D., Giammar, D.E., 2017. Formation, aggregation, and deposition dynamics of nom-iron colloids at anoxic-oxic interfaces. Environ. Sci. Technol. 51, 12235–12245. https://doi.org/10.1021/acs.est.7b02356
Lim, M., Kim, M.J., 2009. Removal of natural organic matter from river water using potassium ferrate(VI). Water. Air. Soil Pollut. 200, 181–189. https://doi.org/10.1007/s11270-008-9902-x
Liu, L., Li, L., Wu, Z., Song, L., 2011. Physiological responses to ferrate (VI) stress in Microcystis aeruginosa. 2011 Int. Conf. Remote Sensing, Environ. Transp. Eng. RSETE 2011 - Proc. 5153–5156. https://doi.org/10.1109/RSETE.2011.5965475
Luh, J., Christenson, E.C., Toregozhina, A., Holcomb, D.A., Witsil, T., Hamrick, L.R., Ojomo, E., Bartram, J., 2015. Vulnerability assessment for loss of access to drinking water due to extreme weather events. Clim. Change 133, 665–679. https://doi.org/10.1007/s10584-015-1493-0
Luo, M., Zhang, H., Zhou, P., Xiong, Z., Huang, B., Peng, J., Liu, R., Liu, W., Lai, B., 2022a. Efficient activation of ferrate(VI) by colloid manganese dioxide: Comprehensive elucidation of the surface-promoted mechanism. Water Res. 215, 118243. https://doi.org/10.1016/j.watres.2022.118243
Luo, M., Zhang, H., Zhou, P., Xiong, Z., Huang, B., Peng, J., Liu, R., Liu, W., Lai, B., 2022b. Efficient activation of ferrate(VI) by colloid manganese dioxide: Comprehensive elucidation of the surface-promoted mechanism. Water Res. 215, 118243. https://doi.org/10.1016/j.watres.2022.118243
Ma, B., Hu, C., Zhang, J., Ulbricht, M., Panglisch, S., 2022. Impact of Climate Change on Drinking Water Safety. ACS Environ. Sci. Technol. Water 2, 259–261. https://doi.org/10.1021/acsestwater.2c00004

Ma, J., Jia, B., Li, S., Kong, Y., Nie, Y., Zhang, H., Xiao, M., Gao, T., 2023. Enhanced coagulation of covalent composite coagulant with potassium permanganate oxidation for algae laden water treatment: Algae and extracellular organic matter removal. Chem. Eng. J. Adv. 13, 100427. https://doi.org/10.1016/j.ceja.2022.100427

Ma, J., Liu, W., 2002. Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation. Water Res. 36, 871–878. https://doi.org/10.1016/S0043-1354(01)00282-2

Ma, J., Loiselle, S., Cao, Z., Qi, T., Shen, M., Luo, J., Song, K., Duan, H., 2023. Unbalanced impacts of nature and nurture factors on the phenology, area and intensity of algal blooms in global large lakes: MODIS observations. Sci. Total Environ. 880, 163376. https://doi.org/10.1016/j.scitotenv.2023.163376

Malmaeus, J.M., Blenckner, T., Markensten, H., Persson, I., 2006. Lake phosphorus dynamics and climate warming: A mechanistic model approach. Ecol. Modell. 190, 1–14. https://doi.org/10.1016/j.ecolmodel.2005.03.017

Marbaniang, C. V., Sathiyan, K., McDonald, T.J., Lichtfouse, E., Mukherjee, P., Sharma, V.K., 2023. Metal ion-induced enhanced oxidation of organic contaminants by ferrate: a review. Environ. Chem. Lett. 21, 1729–1743. https://doi.org/10.1007/s10311-023-01584-4

Matveeva, V.A., Alekseenko, A. V., Karthe, D., Puzanov, A. V., 2022. Manganese Pollution in Mining-Influenced Rivers and Lakes: Current State and Forecast under Climate Change in the Russian Arctic. Water (Switzerland) 14, 1091. https://doi.org/10.3390/w14071091

Niemistö, J., Lund-Hansen, L.C., 2019. Instantaneous Effects of Sediment Resuspension on Inorganic and Organic Benthic Nutrient Fluxes at a Shallow Water Coastal Site in the Gulf of Finland, Baltic Sea. Estuaries and Coasts 42, 2054–2071. https://doi.org/10.1007/s12237-019-00648-5

Sharma, A., 2020. Climate Change Adaptation for Drinking Water Treatment Plant – A case study on Bangkhen Water Treatment Plant. Netw. Water Technol. Asia Pacific. https://doi.org/newtap@jwrc-net.or.jp

Sharma, V.K., Feng, M., Dionysiou, D.D., Zhou, H.C., Jinadatha, C., Manoli, K., Smith, M.F., Luque, R., Ma, X., Huang, C.H., 2022. Reactive High-Valent Iron Intermediates in Enhancing Treatment of Water by Ferrate. Environ. Sci. Technol. 56, 30–47. https://doi.org/10.1021/acs.est.1c04616

Siélliéchi, J.M., Lartiges, B.S., Kayem, G.J., Hupont, S., Frochot, C., Thieme, J., Ghanbaja, J., d'Espinose de la Caillerie, J.B., Barrès, O., Kamga, R., Levitz, P., Michot, L.J., 2008. Changes in humic acid conformation during coagulation with ferric chloride: Implications for drinking water treatment. Water Res. 42, 2111–2123. https://doi.org/10.1016/j.watres.2007.11.017

Skaland, R.G., Herrador, B.G., Hisdal, H., Hygen, H.O., Hyllestad, S., Lund, V., White, R., Wong, W.K., Nygård, K., 2022. Impacts of climate change on drinking water quality in Norway. J. Water Health 20, 539–550. https://doi.org/10.2166/wh.2022.264

Sun, S., Jiang, J., Qiu, L., Pang, S., Li, J., Liu, C., Wang, L., Xue, M., Ma, J., 2019. Activation of ferrate by carbon nanotube for enhanced degradation of bromophenols: Kinetics, products, and involvement of Fe(V)/Fe(IV). Water Res. 156, 1–8. https://doi.org/10.1016/j.watres.2019.02.057

Tien Khoi, T., Thuy An, N., Nhat Huy, N., Thi Thuy, N., 2023. Ferrate as an all-in-one coagulant, oxidant, and disinfectant for drinking water treatment. J. Appl. Water Eng. Res. https://doi.org/10.1080/23249676.2023.2292018

Tobiason, J.E., Bazilio, A., Goodwill, J., Mai, X., Nguyen, C., 2016. Manganese Removal from Drinking Water Sources. Curr. Pollut. Reports 2, 168–177. https://doi.org/10.1007/s40726-016-0036-2

Undurraga, R., Vicuña, S., Melo, O., 2020. Compensating water service interruptions to implement a safe-to-fail approach to climate change adaptation in urban water supply. Water (Switzerland) 12. https://doi.org/10.3390/W12061540

V. Karim, A., Krishnan, S., Pisharody, L., Malhotra, M., 2020. Application of Ferrate for Advanced Water and Wastewater Treatment. Adv. Oxid. Process. - Appl. Trends, Prospect. 1–20. https://doi.org/10.5772/intechopen.90231

Wang, D., Zeng, Z., Zhang, H., Zhang, J., Bai, R., 2022. How does pH influence ferrate(VI) oxidation of fluoroquinolone antibiotics? Chem. Eng. J. 431, 133381. https://doi.org/10.1016/j.cej.2021.133381

Wang, K.M., Shu, J., Wang, S.J., Hong, T.Y., Xu, X.P., Wang, H.Y., 2020. Efficient electrochemical generation of ferrate(VI) by iron coil anode imposed with square alternating current and treatment of antibiotics. J. Hazard. Mater. 384. https://doi.org/10.1016/j.jhazmat.2019.121458

Wu, Z., He, M., Guo, X., Zhou, R., 2010. Removal of antimony (III) and antimony (V) from drinking water by ferric chloride coagulation: Competing ion effect and the mechanism analysis. Sep. Purif. Technol.

76, 184–190. https://doi.org/10.1016/j.seppur.2010.10.006
Zhang, H., Zheng, L., Li, Z., Pi, K., Deng, Y., 2020. One-step Ferrate(VI) treatment as a core process for alternative drinking water treatment. Chemosphere 242, 125134. https://doi.org/10.1016/j.chemosphere.2019.125134
Zhang, X., Feng, M., Luo, C., Nesnas, N., Huang, C.H., Sharma, V.K., 2021. Effect of Metal Ions on Oxidation of Micropollutants by Ferrate(VI): Enhancing Role of FeIVSpecies. Environ. Sci. Technol. 55, 623–633. https://doi.org/10.1021/acs.est.0c04674
Zhao, X.N., Huang, Z.S., Wang, G.J., Liu, Y.L., Song, W.W., Ma, J., Wang, L., 2023. Highly Efficient Utilization of Ferrate(VI) Oxidation Capacity Initiated by Mn(II) for Contaminant Oxidation: Role of Manganese Species. Environ. Sci. Technol. 57, 2527–2537. https://doi.org/10.1021/acs.est.2c06931