Chapter 14

Field Study V: Combined Oxidation Technology Using Ferrates (Fe^{IV-VI}) and Hydrogen Peroxide for Rapid and Effective Remediation of Contaminated Water—Comprehensive Practically Focused Study

Petr Lacina and Michal Hegedüs

Abstract Recently, water-soluble compounds of iron in high oxidation states (Fe^{IV-VI}), also known as ferrates, have gained a lot of attention due to their strong oxidation properties. They can potentially be used for degradation/removal of various compounds from contaminated water. To date, the majority of published papers have concerned only laboratory-scale use of ferrates in model solutions. Large-scale applications of ferrates to remediation have proved so far to be rather complicated as the obtained results failed to meet expectations. Therefore, there is an ongoing need to consider the suitability of their large-scale use. Further combination with other oxidizing agents may provide favorable results. The presented research focuses on laboratory experiments using real groundwater followed by a pilot field application realized as an ex situ experiment and subsequently as in situ remediation. Ferrates were combined with hydrogen peroxide in order to enhance their removal efficiency during this pilot remediation test. Such combination proved to be highly effective achieving 60–80% removal of persistent organic contaminants during the first 24 h.

Keywords Ferrate · Hydrogen peroxide · Iron compounds · Water treatment · Groundwater · Contaminated water · Wastewater · Oxidation technologies · Radical oxidation

---

P. Lacina (✉) · M. Hegedüs
GEOtest, a.s, Brno, Czech Republic
e-mail: lacina@geotest.cz

J. Filip et al. (eds.), *Advanced Nano-Bio Technologies for Water and Soil Treatment*,
Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-3-030-29840-1_14

14.1 Introduction

Over the last two decades, water-soluble compounds of iron in high oxidation states (especially Fe^{V} and Fe^{VI}), also known as ferrates (Sharma et al. 2005; Yates et al. 2014b), have been presented as a promising material for wastewater treatment with an effort to enhance their efficiency. Not only do they possess relatively strong oxidizing properties with the capability of degrading a wide range of organic and inorganic contaminants, but they also provide an environmentally friendly solution for water treatment processes, which is a number-one priority for newly introduced materials on the market. Depending on the reaction conditions, Fe^{VI} (or Fe^{V}) species are reduced to Fe^{III} or Fe^{II}, which in an aqueous environment precipitate out in a form of various polyhydroxy complexes or hydroxides. These compounds are stable forms of iron commonly found in nature (Yates et al. 2014b) and do not represent any potential danger to the environment (Jiang and Lloyd 2002; Sharma 2002, 2011; Sharma et al. 2005; Prucek et al. 2013).

Strong oxidizing properties of ferrates are given by an unusually high oxidation state of iron. In an aqueous environment, ferrates are unstable and are subjected to a rapid reduction to stable forms of iron (see Eqs. 14.1 and 14.2 below). They act as strong electron acceptors, removing electrons from their surroundings. It has been shown that Fe^{VI} can be a stronger oxidant than ozone under specific conditions (Jiang 2014; Jiang et al. 2016). Its redox potential varies from 0.72 V in alkaline medium (Eq. 14.1) to 2.20 V in acidic medium (Eq. 14.2) (Sharma et al. 2005; Tiwari et al. 2006; Prucek et al. 2013; Jiang 2014; Sharma et al. 2014).

$$\mathrm{FeO_4}^{2-} + 4\mathrm{H_2O} + 3\mathrm{e}^- \rightarrow \mathrm{Fe(OH)_3} + 5\mathrm{OH}^- \quad \left(\mathrm{E}^0 = +0.72\ \mathrm{V}\right) \tag{14.1}$$

$$\mathrm{FeO_4}^{2-} + 8\mathrm{H}^+ + 3\mathrm{e}^- \rightarrow \mathrm{Fe}^{3+} + 4\mathrm{H_2O} \quad \left(\mathrm{E}^0 = +2.20\ \mathrm{V}\right) \tag{14.2}$$

The oxidation power of ferrates can be thus altered by adjusting the pH value or by the addition of other oxidizing agents. Ferrates are believed to be an effective remediation material for a wide range of organic (Prucek et al. 2013; Sharma et al. 2014; Yates et al. 2014a; Zhou and Jiang 2015) and inorganic (Filip et al. 2011; Sharma 2011; Machala et al. 2015) contaminants but also as a disinfectant agent (Jiang and Wang 2003; Sharma et al. 2005; Jiang 2014; Sharma et al. 2014; Yates et al. 2014b; Talaiekhozani et al. 2016). On top of that, hydrolysis products of Fe^{III} species in aqueous environments may serve as effective adsorbents of by-products of oxidation processes as well as an effective coagulant and flocculant (Bartzatt et al. 1992; Jiang and Lloyd 2002; Lee et al. 2003; Lee et al. 2009; Filip et al. 2011; Yates et al. 2014b; Talaiekhozani et al. 2016).

However, large-scale utilization of ferrates seems to be less effective than it was previously expected. The pilot studies show big deviances from the results obtained in laboratories. The main drawbacks of their application are as follows:

- they show strong oxidation properties only in acidic environment (lowering the pH value will lead to an increase in the salt content in groundwater)
- under these conditions, they are highly unstable (high amount of ferrates is needed for full remediation)
- in strongly polluted waters, they deteriorate quickly failing to show significant removal efficiency of contaminants

Thus, their efficiency may strongly vary depending on the conditions given by the treated groundwater/wastewater. Their inappropriate application to real waters may end up in a failure. Therefore, there is an ongoing need to consider the suitability of their use or consider their possible combination with other agents (e.g., hydrogen peroxide) to achieve favorable results. It is worth mentioning that a practical application of ferrates should also be preceded by laboratory experiments conducted on particular waters in order to verify the suitability of the proposed process.

The presented research reports on a comprehensive practically oriented study on applications of ferrates in combination with hydrogen peroxide in order to enhance their removal efficiency in remediation of a contaminated real water. On the basis of previously obtained results from laboratory experiments, a field pilot application was realized as an ex situ experiment and subsequently as in situ large-scale remediation in areas of two different industrial factories in the Czech Republic.

14.2 Methods

14.2.1 Materials and Chemicals

Commercial ferrates, ENVIFER, were obtained from NANO IRON, s.r.o. (Czech Republic) in a powder form. It contained iron in high oxidation states as $K_3Fe^{V}O_4$ a $K_2Fe^{VI}O_4$ (total content of Fe 18.4 mass%; content of Fe^{V} 57 ± 3 mol%; content of $Fe^{VI} < 3$ mol%; content of K_2O from production 19 ± 3 mass%). After the product was dissolved in water, Fe^{V} was disproportionate to Fe^{VI} and Fe^{III} (Kokarovtseva et al. 1972; Kolář et al. 2015). The Fe^{VI}/Fe^{V} ratio in water was roughly 0.81. One gram of ENVIFER dissolved in water, thus creating approximately 85 mg of Fe^{VI}. Other used chemicals were as follows: technical hydrogen peroxide 35% (OQEMA, s.r.o., Czech Republic) and sulfuric acid (Chromservis s.r.o., Czech Republic).

14.2.2 Laboratory Tests

Laboratory-scale tests were carried out on real groundwater from two different localities in the Czech Republic, where a pilot field ex situ and in situ application of ferrates was planned. During these experiments, the removal of selected contaminants was studied. Water from locality A was strongly contaminated with chlorinated ethenes (CEs)—total value of CEs (ΣCEs) ranged from 60 to 70 mg/L. Water from locality B was contaminated mainly with benzene, toluene, ethylbenzene, and xylenes (BTEX). The aim of these experiments was to verify and compare the efficiency of ferrates in combination with hydrogen peroxide under various conditions in order to find the most effective method for the pilot application.

During the batch tests, 1000 mL reagent bottles were used. Two parallel sets, each containing six reagent bottles, were prepared. The bottles were labeled sp. 1–6. The first set (labeled A) was prepared with water from locality A, the second set (labeled B) was prepared with water from locality B. Both sets included various combinations of reagents for possible applications. Each of the bottles represented one type of a sample prepared as follows:

sp. 1 Ferrates (0.5 g/L) + pH adjustment ≈ 3 + H_2O_2 (5 mL/L),
sp. 2 Ferrates (0.5 g/L) + H_2O_2 (5 mL/L),
sp. 3 Ferrates (0.5 g/L) + pH adjustment ≈ 3,
sp. 4 Only a dose of ferrates (0.5 g/L),
sp. 5 Only a dose of H_2O_2 (5 mL/L),
sp. 6 Blank

The dose of commercial ferrates was set to 0.5 g/L, which corresponds to the doses of Fe(VI) commonly used for laboratory tests (Prucek et al. 2013). Ferrates were dosed in a powder form and applied directly to the reagent bottle with contaminated groundwater. The bottles were closed and their contents were vigorously mixed with a magnetic stirrer for 30 minutes. Subsequently, the following steps in the selected samples were taken: pH adjustment by 50% H_2SO_4 (sp. 1 and 3) and application of 5 mL hydrogen peroxide (sp. 1, 2, and 5). The closed bottles with the prepared water samples were put on an orbital shaker and were shaken intensively at regular 6-hour intervals for 5 min. Due to the effervescence of the samples (mainly sp. 1 and 2), the lids of the bottles were opened at regular intervals to release accumulated gases. 100 mL of each water sample was collected for analysis after 24, 48, 96, and 168 h and each sample was filtered through a filter paper to remove sludge before analytical sample treatment. The content of contaminants in the samples was analyzed with headspace gas chromatography/mass spectrometry in accredited laboratories. All samples were processed within 24 h of the collection.

14.2.3 Pilot Field Ex Situ Application

Ex situ pilot validation of the obtained laboratory results was carried out in the area of Czech chemical factory, where the groundwater was strongly contaminated with a wide range of organic contaminants. The most important contaminants were as follows: aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes) and chlorinated aromatic hydrocarbons (chlorobenzene, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene). During the initial monitoring process physicochemical analysis of raw groundwater was carried out and the key parameters were determined (Table 14.1). The list of detected contaminants and their concentration levels before the tests are given in Table 14.2.

The pilot application to the target locality as a container test (i.e., ex situ treatment) was carried out in July 2014 using a 1000 liters intermediate bulk container (IBC) made of high-density polyethylene. The container was filled with 900 L contaminated groundwater pumped out from a borehole located in the area of chemical factory surrounding. The whole pilot test consisted of three application steps:

1. 350 g of commercial ferrates (≈ 0.4 g/L ≈ 34 mg Fe^{VI}/L) was applied into the container and the content was then mixed for 15 min.
2. After reduction of all dosed ferrates (visible detection by changing color of water from violet to orange), the first dose of hydrogen peroxide with a volume of 4.5 L (≈ 5 mL/L) was applied. The content of the container was subsequently mixed at 30-min intervals.
3. Four hours after the first application of hydrogen peroxide, the second dose of the same amount 4.5 L H_2O_2 ($\approx$5 mL/L) was applied.

Table 14.1 Qualitative parameters of the raw groundwater

Parameter	Value	Unit
pH	6.29	
Conductivity	4270	μS/cm (20 °C)
Acid-neutralizing capacity ($ACN_{4.5}$)	10.09	mmol/L
Chemical oxygen demand (COD_{Cr})	1090	mg/L
Biochemical oxygen demand (BOD_5)	551	mg/L
Total hardness	8.05	mmol/L
NH^{4+}	37.8	mg/L
Total inorganic nitrogen	10.66	mg/L
Sulfates	855	mg/L
Chlorides	504	mg/L
Nitrates	<3.0	mg/L
Nitrites	<0.10	mg/L
Phosphates	2.92	mg/L
Mineralization	3537	mg/L
Halogenated organic compounds (AOX)	6.42	mg/L

Table 14.2 The list of contaminants detected in groundwater and their concentration level before the start and at the end of the pilot test

Contaminant	Before the start of the test c (μg/L)	At the end of the test c (μg/L)
Benzene	340 ± 85	170 ± 42
Toluene	363,000 ± 90,700	103,000 ± 25,700
∑xylenes	480 ± 120	130 ± 32
1,2,4-trichlorobenzene	62 ± 15	18 ± 4
o-dichlorobenzene	19,000 ± 4700	5800 ± 1400
m-dichlorobenzene	3700 ± 920	970 ± 240
p-dichlorobenzene	4900 ± 1200	1300 ± 320
∑chlorinated ethenes	520 ± 130	<2
Ethylbenzene	140 ± 35	44 ± 11
Chlorobenzene	2900 ± 720	800 ± 200
Naphthalene	3600 ± 900	1200 ± 300
Phenol	3.0 ± 0.7	<2
∑cresols	50 ± 12	220 ± 55
∑dichlorophenols	9 ± 2.2	8.1 ± 2.0
∑chlorophenols	12 ± 3.0	<2
Aniline	730 ± 180	320 ± 80
N-ethylaniline	4.6 ± 1.1	4.2 ± 1.0
2,4,6-trimethylaniline	130 ± 32	<2
Nitrobenzene	2100 ± 520	2300 ± 520

Table 14.3 The time schedule of the pilot test with substantial operations

Time (h)	Operation
0	Filling the container (900 L)
0.75	Application of the ferrate – ENVIFER (350 g)
1.25	Application of 1st dose of H_2O_2 (4.5 L)
5	Application of 2nd dose of H_2O_2 (4.5 L)
24	Termination of the test

The test was terminated after another 19 h. The entire reaction process thus lasted 24 h. Table 14.3 lists a concise time schedule of the pilot test with particular operations. Throughout the test also physicochemical parameters, notably pH, redox potential, and the concentration of dissolved oxygen, were observed and measured by a multiparameter probe Aquaread AP-2000 (Aquaread Ltd., Great Britain).

Simultaneously with the IBC container test, also a blank experiment was realized using 50 L barrel filled with the same groundwater. No oxidizing agents were applied to this barrel, only mechanical and measuring operations (i.e., mixing and measurements of the selected physicochemical parameters) according to the same timetable as in the case of the IBC container (Table 14.3) test were carried out.

14.2.4 Pilot Field In Situ Application

For an in situ pilot validation of results obtained from the laboratory tests, an area of Czech industrial factory aimed at metal production was chosen. Groundwater at this locality was contaminated mainly with CEs. For the pilot verification of results employing the in situ approach, the borehole in strongly contaminated area was chosen. An average level of ΣCEs in this borehole ranged from tens to hundreds mg/L. The in situ pilot application was carried out in three application rounds from February to May 2014. The application procedure was as follows:

1st application round (February 27, 2014)

In the first step, 1500 g of commercial ferrates was dissolved in 700 L of distilled water and the concentrated ferrate solution was applied directly to the application borehole. The water column in the borehole was subsequently mixed by a submersible pump. In the second step, approximately 1 h after the first injection, the pH in the borehole was adjusted to ca value 3 by ca 0.5 L of 50% H_2SO_4. After this, 15 L of 30% H_2O_2 was applied and mixed by submersible pump.

2nd and 3rd application round (March 27 and May 13, 2014)

During these next two application rounds, only 15 L of 30% H_2O_2 was applied.

14.3 Results and Discussion

14.3.1 Results of Laboratory Tests

Groundwater from two different localities (denoted as A and B) was used for the laboratory tests. Both of these localities were selected also for the subsequent pilot test. During the laboratory tests, changes in the concentration of priority contaminants, depending on the reaction time and the type of the prepared sample, were monitored:

- total concentration of CEs (ΣCEs) in the case of locality B (Fig. 14.1)
- total concentration of benzene, toluene, ethylbenzene, and xylenes (ΣBTEX) in the case of locality B (Fig. 14.2)

The zero point on “Reaction time” axis represent initial values, i.e., values of raw water before the start of the test. The graphs in Fig. 14.3 show the overall removal efficiency of the target contaminants after 24 h for each of the prepared samples.

The results obtained from the laboratory tests showed that neither ferrates nor hydrogen peroxide exhibit significant efficiency in the removal of the targeted contaminants, in comparison with the blank (sp. 4, 5, and 6). The reason for the low removal efficiency is high pollution of the tested groundwater, where oxidative effects of ferrates were consumed by easily oxidizable ballast substances present in

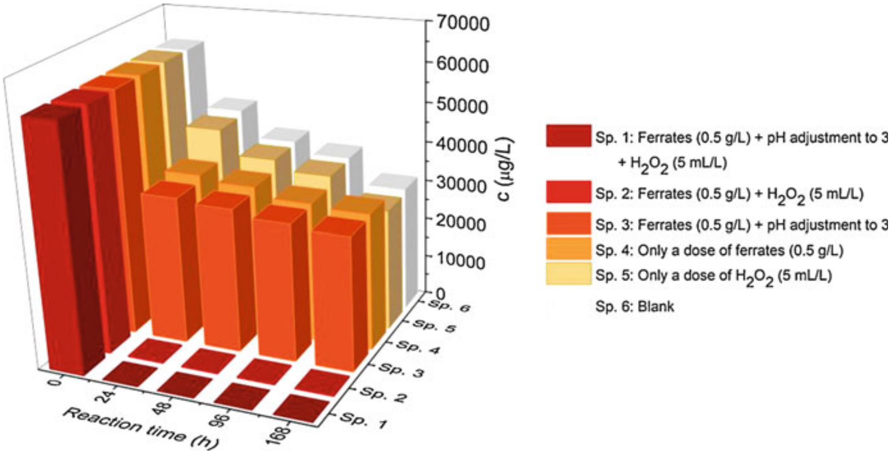


Fig. 14.1 The concentration change of ΣCEs during the laboratory tests (set A)

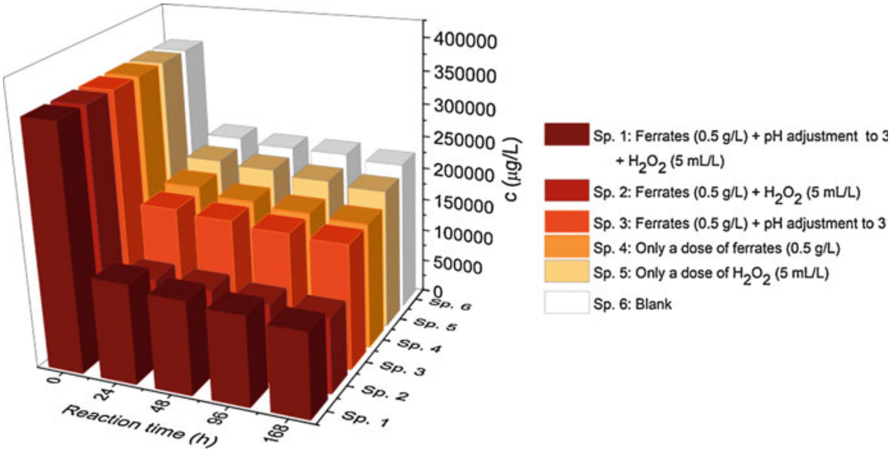


Fig. 14.2 The concentration change of ΣBTEX during the laboratory tests (set B)

the water, and the ferrates degraded too rapidly to be able to degrade the target stable contaminants. Conversely, in samples where only hydrogen peroxide was applied, slow and long decomposition of peroxide without a significant influence on the selected contaminants has been observed. pH adjustment to lower values caused higher degradation of ferrates without a significant effect on the target contaminants—only slight increase in the removal efficiency was observed (sp. 3).

However, the combination of these two agents (sp. 1 and sp. 2) caused a significant increase in the removal efficiency. At the end of the tests on water from locality A, almost 100% efficiency in the removal of the monitored contaminants (CEs) was observed when the pH was not previously adjusted. 60–75% removal efficiency in the selected contaminants (BTEX) was reached in the tests on

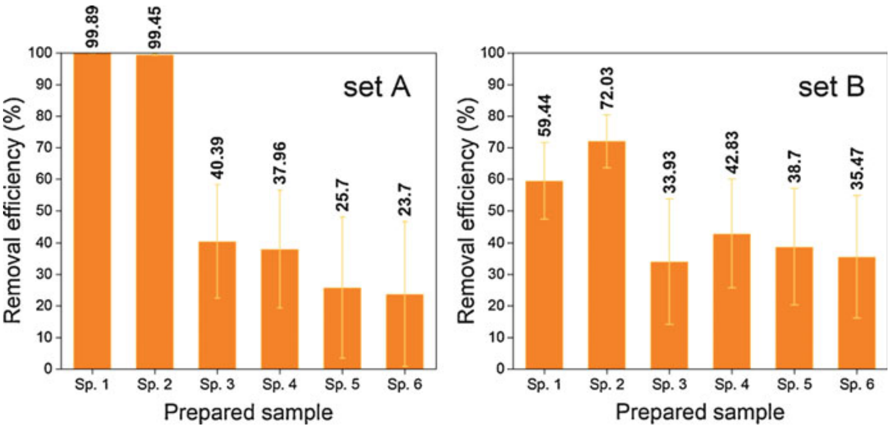


Fig. 14.3 Removal efficiency of target contaminants (ΣCEs of set A and ΣBTEX of set B) after 24-hour reaction time

groundwater from locality B—the highest efficiency in this case was reached without any previous pH adjustment. Both of these reactions (only for sp. 1 and sp. 2) were accompanied by slight fizzing, which was observed until complete decomposition of the applied hydrogen peroxide, detected by starch-iodide papers. The presence of hydrogen peroxide was detected for a maximum of 12–24 h for sp. 1 and sp. 2. In the case of sp. 5, hydrogen peroxide was detected even 96 h after its application. Significantly faster decomposition of hydrogen peroxide in aqueous medium was observed in samples where ferric sludge from gradual ferrate reduction was formed. Such a rapid decrease in the concentration of the target contaminants has been observed only in advanced oxidation processes including radical oxidations by OH radicals (Che et al. 2011; Hrabák 2012; Hara 2012). Considering these facts, it is highly probable that radical oxidation took place in sp. 1 and sp. 2. Characterization of the ferric sludge formed by ferrate reduction gave findings that the sludge comprised of nanostructures, which most likely catalyzed the radical decomposition of hydrogen peroxide. The formed OH radicals then reacted with the target contaminants. This nanoparticle formation after the ferrate addition into natural water was proved by Goodwill et al. (2015). Simultaneously, it was found that the radical reactions were able to run repeatedly after an addition of hydrogen peroxide to the ferric sludge in the water, even without adjusting pH.

14.3.2 Results of Pilot Ex Situ Application

The main aim of the pilot field application was to verify the results from the laboratory experiments in practice. The pilot test was performed as a 24-hour container test carried out directly in the selected area. All substantial operations done during the test are listed in Table 14.3. The design and the implementation of

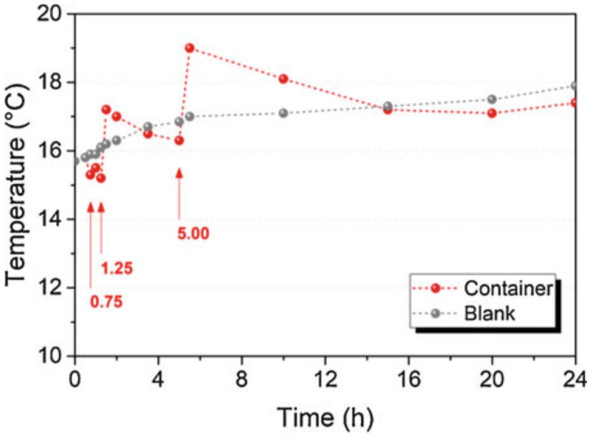
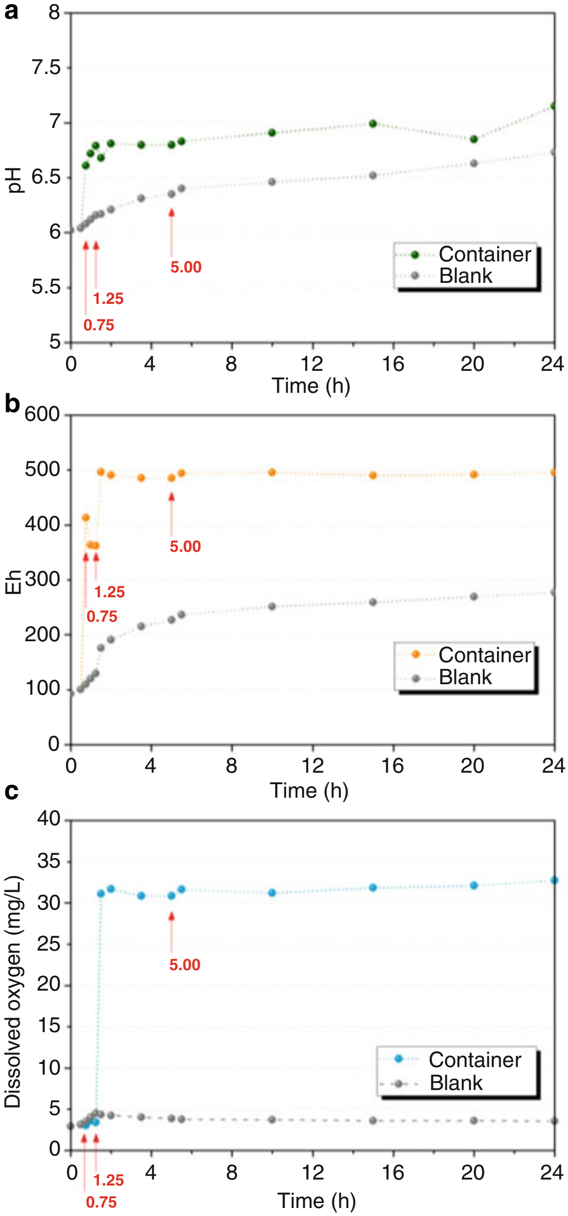


Fig. 14.4 The temperature of water in the reaction container and of the blank sample during the pilot test; the time axis includes times of the applications (corresponding to Table 14.3)

all the operations were based on the findings revealed during the laboratory tests. Raw groundwater pumped into the container was turbid, strongly smelling of organic solvents, and had a gray color. After the first step, i.e., an application of commercial ferrates, color of the raw water rapidly changed to pale orange (within a few minutes) as a consequence of Fe^{3+} ions formation from ferrates reduction. Moreover, this process was associated with the ferric sludge formation (hydrated forms of Fe-oxides) in the form of flakes, which removed the water turbidity and supported sedimentation. After the second step, i.e., hydrogen peroxide application, a gentle fizzing in the whole water volume was observed. Simultaneously, a slight increase in water temperature (ca 2–3 °C) was observed (Fig. 14.4). The effervescence intensity had a decreasing trend during the reaction time along with the temperature of water (Fig. 14.4) and it was no longer observed at the end of the test. Furthermore, the presence of hydrogen peroxide was not detected at the end of the test. After the test terminated, no turbidity was observed, the water was slightly orange, odorless, and the sludge was deposited on the bottom of the container.

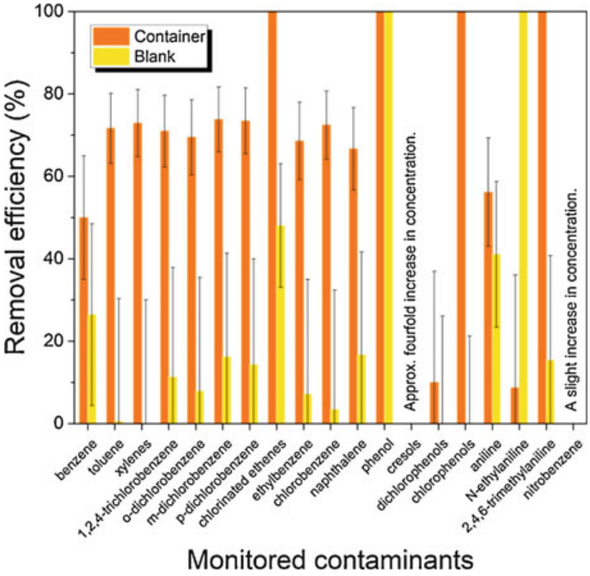
During the test, selected physicochemical parameters (pH, redox potential, dissolved oxygen) were monitored (Fig. 14.5). Expected increase in the pH caused by the reaction of ferrates with water and by presence of K_2O (creating KOH) was observed after the first application step (ferrate application in time 0.75 h). However, due to strong buffering capacity of water, the pH increase was lower than previously expected. Because of this, the pH values were within the optimal range for the formation of ferric sludge flakes, which worked as an effective flocculant. A slight decrease in the pH value occurred after the second application step, i.e., the first dose of hydrogen peroxide (in time 1.25 h), because of its weak acidic effects in an aqueous medium. However, during the reaction time, the pH value returned back due to decomposition of the hydrogen peroxide and buffering capacity of the water. After the third step, i.e., the second dose of hydrogen peroxide (in time 5.00 h), no significant change in the pH values was observed, probably due to degradation products, which contributed to the buffering capacity of the water. In the case of the redox potential (expressed as E_h), significant growth was observed immediately

Fig. 14.5 Evolution of physicochemical parameters in the reaction container and in the blank sample during the pilot test: (**a**) pH, (**b**) redox potential (E_h), (**c**) concentration of dissolved oxygen; the time axis includes times of the applications (corresponding to Table 14.3)



after the first application step (ferrate application in time 0.75 h) and also after the second application step (first dose of hydrogen peroxide in time 1.25 h). Rapid increase in the dissolved oxygen concentration after the second application step was caused by decomposition of dosed hydrogen peroxide. Significant increase in both

Fig. 14.6 Total removal efficiency of monitored contaminants at the end of the pilot test; compared to the blank



redox potential and dissolved oxygen showed the formation of strong oxidizing conditions in the water medium.

Figure 14.5 also shows physicochemical parameters of the blank sample compared with the pilot test. In the case of the blank experiment all measurements were carried out parallel to the measurements carried out during the container test.

The liquid samples for the analysis were prepared in two rounds: (1) just before the start of the test and (2) immediately after its termination. After they were collected, all the samples were transported quickly to accredited laboratories in order to perform sample treatment and analysis. The results of the analysis are listed in Table 14.2. On the basis of the obtained results, the removal efficiency of the pilot test was determined. The overall removal efficiency in the monitored contaminants at the end of the test, i.e., after 24 hours, is listed in Fig. 14.6 including the removal efficiency in the blank sample. All differences between the initial and the final concentrations in the case of the blank sample are results of mixing, aeration, volatilization, sample handling, etc. The obtained results revealed that there was a significant decrease in the concentration of almost all monitored contaminants during the 24-hour pilot test, compared with the blank sample. The removal efficiency in the majority of monitored contaminants ranged between 60 and 80%. Complete elimination was observed with phenol, chlorophenol, N-ethylaniline, and chlorinated ethenes. An increase in the concentration of cresols and nitrobenzene at the end of the test was observed. This is the consequence of radical oxidation reaction (in presence of OH radicals) of selected aromatic compounds in which aromatic alcohols (cresols) can be formed. According to the input data, high concentration of toluene may be primarily responsible for the observed increase. A slight increase in the concentration of nitrobenzene may have resulted from the oxidation of aniline. Zero removal efficiency in Fig. 14.6 means that no changes in the concentrations of selected contaminants were observed during the pilot test, especially in the case of blank: xylenes, cresols, chlorophenols, dichlorophenols, nitrobenzene.

Based on the obtained results of the pilot-field application, the combination of the two oxidizing agents seems to be a promising way for quick removal of a wide range of organic contaminants. It can not only be used for groundwater remediation but also for wastewater and other types of water purification by ex situ methods. Although ferrates used independently in model solutions exhibit strong oxidative effects, they rapidly deteriorate without noticeable effects on chemically stable contaminants in highly polluted real waters. The efficiency of the reaction can be increased by addition of hydrogen peroxide to the formed ferric sludge. The properties of the two reagents can therefore be combined—efficiency of ferrates alone (oxidation, coagulation) and subsequently efficiency of radical oxidation, which is initiated after the addition of hydrogen peroxide to ferric sludge. In this specific case, the formed sludge acts most likely as a catalyst for radical degradation of hydrogen peroxide. Therefore, the removal efficiency is comparable to the Fenton oxidation. On top of that, ferrates utilization does not lead to increased salinity of water and no other substances are introduced to an aqueous environment (as sulfates, acids, etc.). From the viewpoint of the environmental protection, the proposed combination represents no risk—ferrates are reduced to Fe^{3+}/Fe^{2+} and precipitate in the form of polyhydroxy complexes and hydroxides, which commonly occur in nature, and hydrogen peroxide is degraded to O_2 and H_2O.

14.3.3 Results of Pilot In Situ Application

The purpose of this type of ferrate application was to verify the results obtained from the laboratory experiment employing the method of in situ remediation. It is necessary to emphasize that the pH was adjusted only before the first application round; in another application round, only H_2O_2 was added into the application borehole. The reason for this step was to verify if the remaining ferric sludge, which was detected in the borehole even during the second and the third application round, would react with a new dose of hydrogen peroxide even without pH adjustment. After all applications of hydrogen peroxide, the reaction in the borehole was relatively tempestuous, but it lasted only a few hours. Between all application rounds, regular monitoring was carried out. In the following graphs (Fig. 14.7a–c) physicochemical parameters are shown. It is obvious that rapid increase in the E_h and dissolved oxygen (DO) was observed after the application in all cases, as a consequence of H_2O_2 decomposition. Decrease in the pH was also observed in all cases. In the first application round it was the consequence of target pH adjustment. In other application rounds, when the pH was not adjusted, it was the result of acidic nature of H_2O_2 itself.

According to the graph showing CE contamination development (Fig. 14.7d), it is obvious that a rapid decrease was observed after each application. It made no

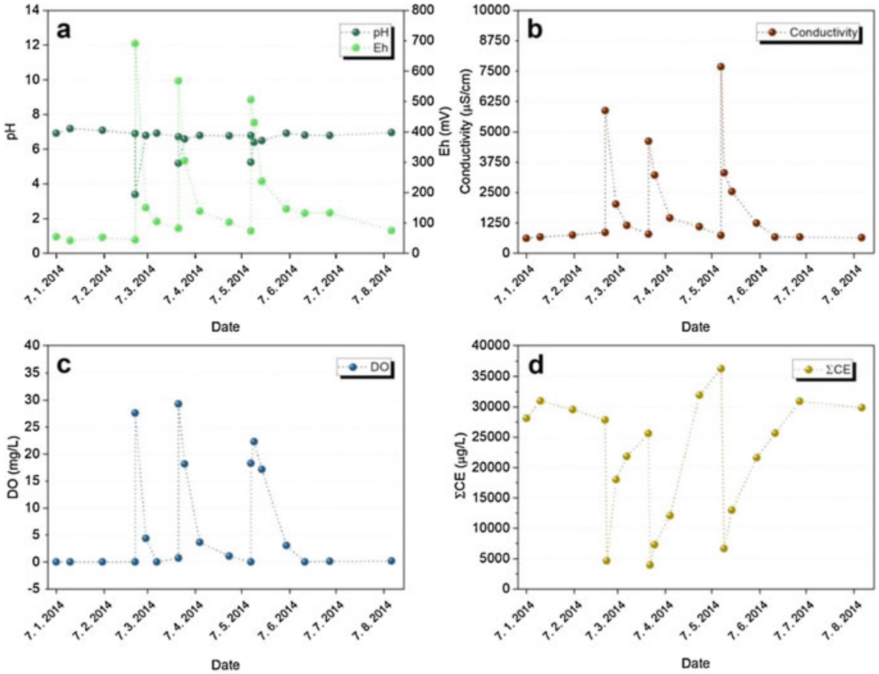


Fig. 14.7 (**a–c**) Evolution of physicochemical parameters of pilot in situ application and (**d**) CEs concentration development in time

significant difference whether the pH was adjusted or not. On the basis of the obtained results, also in the case of in situ application, it was proved that a radical reaction with ferric sludge from ferrate reduction ran even without pH adjustment. However, a rapid increase in the contamination was observed during in situ remediation as a consequence of contamination subsidy from contaminated soil surroundings. This represents a significant difference between in situ and ex situ application. Therefore, in the case of in situ application it is necessary to apply hydrogen peroxide repeatedly at short intervals. The only condition is the presence of ferric sludge from ferrate reduction in the borehole. A major advantage of this approach is the use of hydrogen peroxide solely. Compared to the Fenton oxidation, there is no need for pH adjustment and repeated addition of ferrous sulfate, so there is no salinization of the rock environment.

14.4 Conclusions

The use of ferrates alone during the remediation of heavily contaminated groundwater and wastewater does not seem to provide expected results. Therefore, it is inevitable to reexamine other options for their use (e.g., further purification, coagulation, flocculation, disinfection, etc.) or their use in a combination with other agents, which will assist in achieving the expected effectiveness in remediation practice. One of the options is their combination with hydrogen peroxide, where nanostructured ferric/ferrous sludge is formed by the reduction of ferrates. This sludge can act as an effective catalyst for radical decomposition of hydrogen peroxide. The aim of this study was to test the combination of ferrates with hydrogen peroxide in laboratory conditions and then to realize a field pilot application. The proposed combination showed a relatively high efficiency during remediation of even heavily contaminated water. Ferrates were finally reduced to naturally occurring forms of iron and the final products of the hydrogen peroxide degradation were oxygen and water. Thus, no other contaminants were discharged into the aqueous environment. No increase in salinity of the water was observed either. The reaction proceeded rapidly even without pH value adjustment or other parameters of the reaction being changed. In addition to this, the formed iron sludge acted as an effective flocculant. The presence of this sludge in purified water is the necessary condition for the successful remediation by subsequent hydrogen peroxide application. Comparing ex situ and in situ applications, the removal efficiency is high in both cases, but significant difference consists in the rapid run of the reaction. In the case of water remediation by an ex situ method, this is an advantage as the effective remediation during short time is required. Conversely, in the case of water remediation by an in situ method, this is a disadvantage because the contamination returns rapidly to the initial level as a consequence of contamination of the soil surrounding. In this case, rather long-term remediation reactions are required.

References

Bartzatt R, Cano M, Johnson L, Nagel D (1992) Removal of toxic metals and nonmetals from contaminated water. J Toxicol Environ Health 35(4):205–210. https://doi.org/10.1080/15287399209531611

Che H, Bae S, Lee W (2011) Degradation of trichloroethylene by Fenton reaction in pyrite suspension. J Hazard Mater 185(2–3):1355–1361. https://doi.org/10.1016/j.jhazmat.2010.10.055

Filip J, Yngard RA, Siskova K, Marusak Z, Ettler V, Sajdl P, Sharma VK, Zboril R (2011) Mechanisms and efficiency of the simultaneous removal of metals and cyanides by using ferrate(VI): crucial roles of nanocrystalline iron(III) oxyhydroxides and metal carbonates. Chem Eur J 17(36):10097–10105. https://doi.org/10.1002/chem.201100711

Goodwill JE, Jiang Y, Reckhow DA, Gikonyo J, Tobiason JE (2015) Characterization of particles from ferrate preoxidation. Environ Sci Technol 49(8):4955–4962. https://doi.org/10.1021/acs.est.5b00225

Hara J (2012) Chemical degradation of chlorinated organic pollutants for in situ remediation and evaluation of natural attenuation. In: Puzyn T, Mostrag-Szlichtyng A (eds) Organic pollutants ten years after the Stockholm convention – environmental and analytical update. InTech, Rijeka, pp 345–364. https://doi.org/10.5772/31775

Hrabák P (2012) Kritické studium sanačního využití modifikovaného Fentonova činidla (A critical study of remedial utilization of modified Fenton reagent). Dissertation, Technical University of Liberec

Jiang JQ (2014) Advances in the development and application of ferrate(VI) for water and wastewater treatment. J Chem Technol Biotechnol 89(2):165–177. https://doi.org/10.1002/jctb.4214

Jiang J-Q, Lloyd B (2002) Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. Water Res 36(6):1397–1408. https://doi.org/10.1016/S0043-1354(01)00358-X

Jiang J-Q, Wang S (2003) Inactivation of Escherichia coli with ferrate and sodium hypochlorite: a study on the disinfection performance and constant. In: Vogelpohl A (ed) Proceedings of the 3rd international conference on oxidation technologies for water and wastewater treatment, Goslar, 18–22 May 2003, CUTEC-Series Publication No. 57. Papierflieger Verlag, Clausthal-Zellerfeld, pp 403–411

Jiang JQ, Durai HBP, Petri M, Grummt T, Winzenbacher R (2016) Drinking water treatment by ferrate(VI) and toxicity assessment of the treated water. Desalin Water Treat 57 (54):26369–26375. https://doi.org/10.1080/19443994.2016.1203825

Kokarovtseva IG, Belyaev IN, Semenyakova LV (1972) Oxygen compounds of iron(VI, V, IV). Russ Chem Rev 41(11):929–937. https://doi.org/10.1070/RC1972v041n11ABEH002104

Kolář M, Kolařík J, Jančula D, Slunský J, Medřík I, Filip J, Maršálek B, Zbořil R (2015) Feráty: vlastnosti a přehled možných environmentálních aplikací (ferrates: properties and the overview of possible environmental applications). In: Burkhard J, Petráková Kánská K (eds) Sanační technologie XVIII, Uherské Hradiště, 19–21 May 2015, pp 152–154

Lee Y, Um I-h, Yoon J (2003) Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation. Environ Sci Technol 37(24):5750–5756. https://doi.org/10.1021/es034203+

Lee Y, Zimmermann SG, Kieu AT, von Gunten U (2009) Ferrate (Fe(VI)) application for municipal wastewater treatment: a novel process for simultaneous micropollutant oxidation and phosphate removal. Environ Sci Technol 43(10):3831–3838. https://doi.org/10.1021/es803588k

Machala L, Filip J, Prucek R, Tucek J, Frydrych J, Sharma VK, Zboril R (2015) Potassium ferrite ($KFeO_2$): synthesis, decomposition, and application for removal metals. Sci Adv Mater 7 (3):579–587. https://doi.org/10.1166/sam.2015.2143

Prucek R, Tuček J, Kolařík J, Filip J, Marušák Z, Sharma VK, Zboril R (2013) Ferrate(VI)-induced arsenite and arsenate removal by in situ structural incorporation into magnetic iron(III) oxide nanoparticles. Environ Sci Technol 47(7):3283–3292. https://doi.org/10.1021/es3042719

Sharma VK (2002) Potassium ferrate(VI): an environmentally friendly oxidant. Adv Environ Res 6 (2):143–156. https://doi.org/10.1016/S1093-0191(01)00119-8

Sharma VK (2011) Oxidation of inorganic contaminants by ferrates (VI, V, and IV)-kinetics and mechanisms: a review. J Environ Manag 92(4):1051–1073. https://doi.org/10.1016/j.jenvman.2010.11.026

Sharma VK, Kazama F, Jiangyong H, Ray AK (2005) Ferrates (iron(VI) and iron(V)): environmentally friendly oxidants and disinfectants. J Water Health 3(1):45–58. https://doi.org/10.2166/wh.2005.0005

Sharma VK, Homonnay Z, Siskova K, Machala L, Zboril R (2014) Mössbauer investigation of the reaction of ferrate(VI) with sulfamethoxazole and aniline in alkaline medium. Hyperfine Interact 224(1–3):7–13. https://doi.org/10.1007/s10751-013-0819-4

Talaiekhozani A, Bagheri M, Talaei MR, Jaafarzadeh N (2016) An overview on production and applications of ferrate(VI). Jundishapur J Health Sci 8(3):e34904

Tiwari D, Kim H-U, Lee S-M, Yang J-K, Kim H (2006) Ferrate(VI) for waste water treatment : oxidation of cyanide in aqueous medium. Environ Eng Res 11(6):318–324. https://doi.org/10.4491/eer.2006.11.6.318

Yates BJ, Darlington R, Zboril R, Sharma VK (2014a) High-valent iron-based oxidants to treat perfluorooctanesulfonate and perfluorooctanoic acid in water. Environ Chem Lett 12 (3):413–417. https://doi.org/10.1007/s10311-014-0463-5

Yates BJ, Zboril R, Sharma VK (2014b) Engineering aspects of ferrate in water and wastewater treatment – a review. J Environ Sci Health Part A 49(14):1603–1614. https://doi.org/10.1080/10934529.2014.950924

Zhou Z, Jiang J-Q (2015) Reaction kinetics and oxidation products formation in the degradation of ciprofloxacin and ibuprofen by ferrate(VI). Chemosphere 119:S95–S100. https://doi.org/10.1016/j.chemosphere.2014.04.006