Chapter 8
Ferrates as Powerful Oxidants in Water Treatment Technologies

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Abstract Over the past decades, soluble compounds with iron in high oxidation state(s) (so-called ferrates) have turned out to be a highly promising and “green” oxidants deployed in water treatment technologies. Ferrates(IV, V, VI) have good oxidation properties, as indicated by the magnitude of the oxidation-reduction potential (an acidic reaction with an oxidation-reduction potential of 2.20 V, in the basic environment it is 0.72 V), making them interesting for oxidation of inorganic compounds including metals, the decomposition of broad range of organic pollutants including various types of micropollutants found in wastewater (pesticides, pharmaceuticals, and drugs), and for disinfection. The important advantage of ferrates is also their minimal environmental load as the reactions result in the formation of benign iron hydroxides. The only limitation of using ferrates in practice is their demanding production as well as their instability due to the high electron affinity of hexavalent iron.

Keywords Iron · High-valent states · Ferrates · Synthesis · Organic pollutants · Micropollutants · Pharmaceutical compounds · Heavy metals · Arsenic · Coagulation · Disinfection

8.1 Introduction

The occurrences of diverse emerging contaminants (heavy metals, volatile organic carbons, pesticides, personal care products, pharmaceuticals, organics, illicit drugs, and pathogenic microbes), particularly in soil and groundwater, have a negative impact on the environment. Therefore, the contamination of ground and surface

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water with various pollutants has been recognized as a global problem that needs cost-effective and environmentally friendly solution(s). One of the ways to overcome the above-mentioned problem is to use ferrate(VI) that offers desirable chemical properties, such as extremely high redox potential (+2.2 V in acidic and + 0.7 V in alkaline solution, respectively) and benign reaction product(s). Thanks to these unique properties, ferrate(VI) is able to eliminate microorganisms, viruses, inorganic, and organic (both natural and synthetic) compounds (Jiang and Lloyd 2002; Kubiňáková et al. 2017; Mackul'ak et al. 2016; Rai et al. 2018).

The most common oxidation states in which iron can be usually found are Fe(0), Fe(II), and Fe(III). Other, unusually high oxidation states, e.g., +IV, +V, and +VI, have also been observed $[Fe^{VI}O_4]^{2-}$. The first mention of ferrates(VI) dates back to 1702. Later on, in 1715, K_2FeO_4 was prepared by oxidation of iron in molten KNO_3. During the smelting of iron ore with potassium carbonate and after the dissolution of residues in alkaline solution, the violet coloration was observed. Some researchers assumed that the violet color of this product was caused by the presence of $Fe^{VI}O_3{}^{-II}$ compound (Mácová et al. 2009). In an aqueous environment, ferrates(VI) possess dark violet color and the ion $[Fe^{VI}O_4]^{2-}$ has tetrahedral structure (Jiang and Lloyd 2002).

A lot of new information has emerged in the literature over the past years relating to the preparation of ferrate(VI), its application to the removal of various organic, inorganic compounds, radionuclides, and the mechanism of ferrate action (Feng et al. 2016; Híveš et al. 2016; Jiang and Lloyd 2002; Jiang 2014; Kralchevska et al. 2016a; Kubiňáková et al. 2015a, b; Mackul'ak et al. 2016; Rai et al. 2018; Sharma et al. 2016a, b). In this chapter, we summarize the current knowledge of a ferrate synthesis using various reaction routes, ferrate stability, and applicability to the elimination of broad range of inorganic and organic compounds. The disinfection properties of ferrates are also mentioned.

8.2 Synthesis of Ferrates(IV, V, VI)

There are several approaches to synthetizing potassium ferrate(VI) (K_2FeO_4), potassium ferrate(V) (K_3FeO_4), and sodium ferrate(IV) (Na_4FeO_4) (Mura et al. 2017; Sharma et al. 2015). Particularly wet chemical methods, electrochemical methods, and thermal processes (Fig. 8.1) are used. When selecting a suitable method of synthesis, it is necessary to consider its experimental difficulty and compromise between purity and the amount of the as-prepared ferrate. Generally, wet chemical synthesis and electrochemical synthesis result in a high-purity ferrate sample, but the amounts of the synthesized material are relatively low. Therefore, such an approach is not suitable for large-scale production, i.e., application of ferrates to water treatment. On the other hand, thermal syntheses enable to prepare much higher amounts of ferrates (up to kilograms per one synthetic cycle), but their purity is relatively low (approx. 30–50 wt.% of K_2FeO_4 in sample) mainly due to self-decomposition of ferrates at high temperatures.

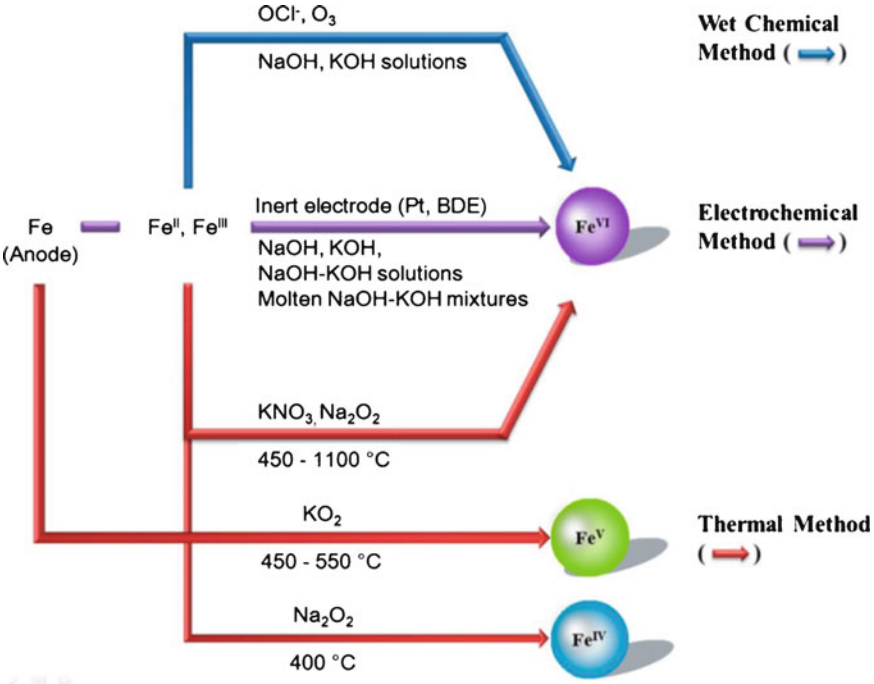


Fig. 8.1 Possible approaches to the synthesis of ferrates. (Reprinted with permission from Sharma et al. (2015). Copyright (2015) American Chemical Society)

Potassium ferrate(VI) (K_2FeO_4) as the most often applied ferrate or sodium ferrate(VI) (Na_2FeO_4) can be prepared by a wet chemical synthesis. Iron(III) oxides or their salts (e.g., ferric chloride or potassium nitrate) are oxidized by hyperchlorite ion (OCl^-) in highly alkaline solution, prepared by NaOH resulting in sodium ferrate (VI) according to the following reaction:

$$2Fe(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2Fe^{VI}O_4 + 3NaCl + 5H_2O \tag{8.1}$$

Potassium ferrate(VI) can then be obtained through precipitation from the solution of Na_2FeO_4 by adding KOH according to the reaction:

$$Na_2Fe^{VI}O_4 + 2KOH \rightarrow K_2Fe^{VI}O_4 + 2NaOH \tag{8.2}$$

The purity of ferrates prepared by this method is very high (approx. 98%). However, it is worth mentioning that this wet chemical method of synthesis is not environmentally friendly as it results in high concentrations of NaOH and residues of NaOCl in reaction solutions.

Concerning a wet chemical approach, the electrochemical anodic oxidation of iron or cast iron in concentrated hydroxide solutions or melts provides much more environmentally friendly process employing an iron electrode (Fe(0)), salts of Fe (II) or Fe(III), and/or iron oxides. In the case of a melt, a suitable temperature for ferrate(VI) synthesis is up to 200 °C. Generally, in aqueous solutions, temperatures range from 20 to 70 °C (Mácová et al. 2009). Using electrochemical methods, high-purity ferrates are easily prepared. The drawback of the method lies in the overlap of potentials of the oxidation of Fe(III) to Fe(VI) and oxygen evolution. The yield of the synthesis depends on temperature, composition of the iron precursors, and the pH of the alkaline solution. As an example, the electrochemical synthesis of ferrate (VI) was studied in a eutectic NaOH-KOH molten salt and in a highly alkaline mixed NaOH-KOH aqueous solution (Híveš et al. 2008). Moreover, electrochemical *DC* (direct current) and *AC* (alternating current) techniques were found to be suitable for interfacial and metal dissolution studies in both aqueous and molten systems (Híveš et al. 2016). Transpassive iron dissolution in alkaline solutions is discussed less frequently. It has been found that in an alkaline environment, Fe is dissolved as ferrous(II), ferric(III) and, finally, ferrate(VI) species depending on the experimental conditions (Híveš et al. 2008, 2014, 2016; Hrnčiariková et al. 2013; Kerekeš et al. 2014; Kubiňáková et al. 2015a, b; Mácová et al. 2009; Rai et al. 2018; Sun et al. 2016; Yu and Licht 2008).

Thermal processes were applied to synthesize sodium ferrate(IV) (Na_4FeO_4), potassium ferrate(V) (K_3FeO_4), or potassium ferrate(VI) (K_2FeO_4). Sodium ferrate (IV) can be prepared by a solid-state reaction of Fe_2O_3 and Na_2O_2 powders mixed in the theoretical molar ratio of Fe:Na = 1:2 (nevertheless an excess of Na_2O_2 in the mixture is recommended to achieve complete oxidation of Fe_2O_3 within the sample) according to the reaction:

$$\mathrm{Fe_2O_3 + 3Na_2O_2 \rightarrow 2Na_2FeO_4 + Na_2O} \tag{8.3}$$

The homogeneous mixture is heated at 400 °C for 1 h. When using a stream of oxygen during the synthesis, the temperature of 370 °C is sufficient. After annealing, the crucible containing the sample must be rapidly cooled down. The purity of Fe (IV) is more than 90%. It is highly recommended to carry out the synthesis in a glove box since both the sodium peroxide precursor and the sodium ferrate(IV) product are highly hygroscopic. Even Mössbauer spectroscopy analysis, which is typically used for verification of the purity of the as-prepared samples, is recommended to be conducted directly in the glove box (Fig. 8.2).

Potassium ferrate(V) (K_3FeO_4) can be synthesized by a two-step solid state reaction starting from homogenous mixture of Fe(III) hydroxide and KNO_3 (Machalová Šišková et al. 2016) with almost equal weights (e.g., several grams). In the first reaction step, the mixture was put into a corundum annealing crucible and the crucible was covered with a lid. The closed crucible was then put into the furnace and annealed at 950 °C for 30 min. After it was annealed, the closed crucible was removed from the furnace and put into a desiccator where it was left to cool down with $KFeO_2$ as a resulting product. Then the as-synthesized $KFeO_2$ was added to KNO_3 powder. Again, the mixture was homogenized in the grinding mortar. The homogenized mixture was then put into a corundum annealing crucible and was

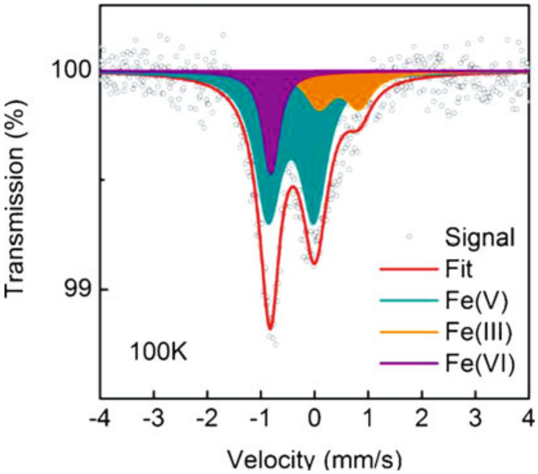
Fig. 8.2 A glove box with a furnace for the synthesis of sodium ferrate(IV). A room temperature Mössbauer spectrometer is installed directly inside the glove box (white tube on the right side)

covered with a lid. The crucible was then put into the furnace and annealed at 1000 °C for 30 min at an N_2 flow of 150 L/h. Before the termination of annealing, another metallic annealing crucible was cooled by liquid nitrogen; afterwards, liquid nitrogen was poured to the crucible. After removing the crucible from the furnace, the melt was poured into the crucible filled with liquid nitrogen. The as-prepared K_3FeO_4 is stable below the level of liquid nitrogen. After it was frozen, K_3FeO_4 was transferred to a porcelain dish with nitrogen and was put into a glove box. Again, more than 90% of Fe(V) (atomic percent of Fe) can be achieved. When the mixture of Fe(III) oxide and KNO_3 is heated at 1100 °C, potassium ferrate(VI) (K_2FeO_4) can be prepared; however, it will yield only 30% purity.

8.3 Experimental Methods for the Characterization of As-Prepared Ferrates and Determination of Their Purity

The relative amount of a ferrate in liquid and solid phases can be determined by using a variety of different analytical techniques (Mura et al. 2017; Sharma et al. 2015), such as volumetric, electrochemical (cyclic voltammetry and potentiometry), and spectroscopic techniques (Fourier-transform infrared spectroscopy—FTIR, ^{57}Fe Mössbauer spectroscopy). The concentration of ferrates in the solution can be

Fig. 8.3 A typical Mössbauer spectrum of Fe (VI), Fe(V), and Fe(III) species formed together during a transformation of ferrate(V) in ethanol. The sample was treated by rapid-freeze technique and spectrum measured at 100 K



monitored by UV-VIS spectrometry. The key experimental tool for characterization of solid samples of ferrates is Mössbauer spectroscopy on isotope ^{57}Fe. The method is selective to the Fe element so it is a unique tool for identification/characterization of Fe-containing phases. Importantly, Mössbauer spectroscopy is sensitive to valence state of iron through isomer shift value as one of the hyperfine parameter. Particularly, Fe(V) and Fe(VI) atoms show negative isomer shift values, which are very different from common Fe(II) or Fe(III) states (see Fig. 8.3). Ferrate samples often contain Fe(III) admixtures, which are amorphous and/or nanocrystalline. Low temperature and external magnetic field Mössbauer spectroscopy provide very detailed characterization of these Fe(III) phases. Even though Mössbauer spectroscopy is designed for characterization of solid samples, it is possible to analyze frozen solutions as well. Relative areas of the spectral components correspond to relative amounts of corresponding Fe-containing phases. It is worth mentioning that these relative amounts are expressed in atomic percent of Fe atoms. Therefore, the values must be recalculated when we need mass ratios of the phases (moreover, chemical formulas of the phases are needed).

8.4 Stability of Solid Ferrates at High Temperatures and in a Humid Air

The issue of thermal stability of ferrates is crucial for the thermal synthesis as well as for possible applications at elevated temperatures. Generally, the instability of ferrates at high temperatures significantly decreases yield and purity of ferrates prepared the thermal processes. The focus will now be shifted to the mostly used ferrate(VI), K_2FeO_4. A thorough study conducted by Machala et al. (2007) showed that potassium ferrate(VI) starts to decompose above 190 °C towards potassium ferrite ($KFeO_2$) and potassium oxides. After it is cooled down to room temperature, $KFeO_2$ becomes unstable and reacts with air H_2O and CO_2 with the formation of Fe_2O_3 nanoparticles and $KHCO_3$ carbonate (Machala et al. 2015a). Conventional experimental techniques confirmed the presence of neither Fe(V) nor Fe (IV) intermediates during the thermal decomposition of ferrates. A later study (Machala et al. 2015b) employing nuclear forward scattering of the synchrotron radiation proved the presence of several percent of Fe(IV) and Fe(V) during the decomposition of potassium ferrate(VI).

From the point of view of storage and handling of ferrates, the issue of stability of potassium ferrate(VI) in air at room temperature is crucial as well. In the study of Machala et al. (2009), the kinetics of solid-state transformation (aging) of potassium ferrate(VI) under various air-humidity conditions (55–95% relative humidity) at room temperature were studied by in situ ^{57}Fe Mössbauer spectroscopy. The kinetic data showed a significant increase in the decomposition rate with increasing air humidity (Fig. 8.4). Crystals of $KHCO_3$ and amorphous $Fe(OH)_3$ nanoparticles were identified as the transformation products. The decomposition kinetics was very unusual with two almost linear decay steps in case of lower humidity levels (55–70%). The first slow decay was probably observed due to the formation of the narrow compact layer of nanoparticulate $Fe(OH)_3$ reaction product. This layer limits the access of both H_2O and CO_2 participating in the reaction as the gaseous reactants. The second decay with a much faster rate showed a nearly positive linear relationship with the humidity.

8.5 Stability of Ferrates in Aqueous Solution

For applications of ferrates to water treatment, an aqueous solution of dissolved ferrate at a certain concentration should be usually prepared in advance. Therefore, it is necessary to know the kinetics and mechanism of ferrates' self-decay in water under different conditions. Stability of ferrates in water depends on many factors such as ferrate concentrations, pH, temperature, or presence of inorganic ions. Generally, ferrates tend to reduce to Fe(III) and/or charge disproportionation takes place. Concerning ferrate(VI), after it is dissolved in water, 5–10% of the ferrate are decomposed to Fe(III) immediately (during 1–2 s). From the literature (Lee et al. 2014), it is known that ferrate(VI) undergoes a dimerization process with Fe(IV) as an intermediate state; however, this reaction is probably too fast to identify Fe(IV) by conventional experimental techniques. The reduction of ferrate(VI) is accompanied by evolution of oxygen and increasing of pH up to 13. During the several-minute-long ferrate(VI) transformation in water, the pH value decreases slowly to approx. 10 and the content of ferrate(VI) slightly decreases by approx. 3%. Just before its application to water treatment, it is necessary to decrease pH in order to have almost neutral conditions along with enhancing the reactivity of the ferrate. The transformation of potassium ferrate(VI) in water can be described by chemical equation

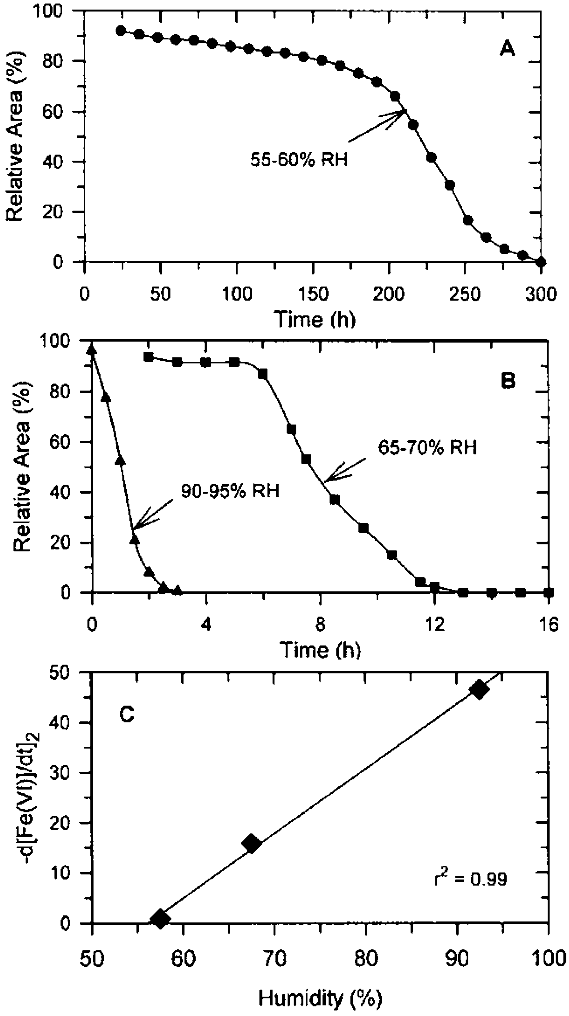


Fig. 8.4 Kinetics of transformation of solid potassium ferrate(VI) at room temperature in air expressed as dependence of Mössbauer spectral area of the ferrate subspectrum on the relative humidity ((**a**) lowest *RH*; (**b**) higher *RH* levels; (**c**) dependence of the second step decay rate on the relative humidity). (Reprinted with permission from Machala et al. (2009). Copyright (2009) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

$$2K_2FeO_4 + 5H_2O \rightarrow 2Fe(OH)_3 + 4KOH + 3/2O_2 \tag{8.4}$$

Dissolving ferrate(V) in water leads to fast disproportionation of Fe(V) into Fe (III) and Fe(VI). Formation of Fe(IV) during the process was not confirmed. Charge disproportionation and reduction of the ferrate compete in the process; therefore, the Fe(III)/Fe(VI) ratio is not typically 1:2 but quite close to 1:1. Thus, the transformation can be described by chemical equation

$$2K_3FeO_4 + 3/2H_2O \rightarrow KFeO_2 + K_2FeO_4 + 3KOH + 1/4O_2 \tag{8.5}$$

The formation of Fe(VI) during the transformation of ferrate(V) in water has an important application aspect. As it has been already mentioned, potassium ferrate (V) can be synthesized by the solid-state method on a large scale (contrary to ferrate (VI)). But after ferrate(V) is dissolved in water, the final oxidizing agent is Fe(VI).

Concerning sodium ferrate(IV), after it has been dissolved in water, immediate transformation to Fe(III) takes place. The process is accompanied by rapid increase of pH up to 13 and evolution of oxygen. The corresponding chemical equation describing the transformation can be written as

$$\mathrm{Na_4FeO_4} + 3/2\mathrm{H_2O} \rightarrow \mathrm{NaFeO_2} + 3\mathrm{NaOH} + 1/4\mathrm{O_2} \tag{8.6}$$

It is worth mentioning that due to this rapid decay, the applicability of sodium ferrate(IV) to water treatment is very limited. This was confirmed, e.g., in the study by Machalová Šišková et al. (2016), where very low efficiency in the degradation of estrogenic hormones was observed in case of sodium ferrate(IV), in comparison with potassium ferrates(V) or (VI).

8.6 Effect of Buffering Inorganic Ions on Stability of Ferrates

The study by Kolář et al. (2016) provided a systematic kinetics investigation of the decay of ferrate(VI) in the presence of inorganic buffering ions (borate, phosphate, and carbonate) at a pH range from 6.0 to 9.0. Detailed kinetic analysis revealed that carbonate anion enhanced the Fe(VI) transformation rate, compared to phosphate and borate ions. The order of the Fe(VI) decay rate in neutral solution condition was carbonate > phosphate $\geq$ borate. In alkaline solution, the decay rates of Fe(VI) were similar for the studied buffering ions. The results indicated that carbonate ions induced the formation of ultrasmall iron(III) oxyhydroxide nanoparticles (<5 nm), which contributed to the increased decay of Fe(VI) because of their larger specific surface area, where the catalytic reactions took place. On the other hand, the observed low reactivity of borate with Fe(VI) demonstrates that borate is the least reactive buffer for studies of Fe(VI) reactivity in neutral solutions.

8.7 Degradation of Organic Pollutants by Ferrate

One of the fresh challenges in water treatment is to develop new methods for elimination of organic pollutants, especially for persistent compounds. Various conventional methods such as adsorption, filtration, sedimentation, oxidation processes, and photocatalytical methods require relatively high operational costs and yield inadequate efficiency. Moreover, currently the emphasis is put on green technologies employing environmentally friendly agents and chemicals used during the processes. Monitoring intermediates and residuals of pollutants as well as testing toxicity of the final products of reactions are more and more required. In this way, ferrates represent effective and promising agents for water treatment of various organic pollutants.

The majority of studies on organic pollutants degradation by ferrates focuses on the use of ferrate(VI). This is a sensible approach because the stability of high-valent iron species in a water solution is dramatically different. While ferrate(VI) is relatively stable, from minutes to days, depending on the solution composition and physicochemical conditions, ferrate(IV) and ferrate(V) decay in seconds resulting in an already mentioned stable ferrate(VI) and trivalent iron products. Hence, ferrate (VI) reacts with organic pollutants although the primary oxidative agents used at the beginning were ferrate(IV) or ferrate(V). This also plays its role in focusing on iron (VI) within ferrate research. On the other hand, it is a well-known fact that ferrate (V) is more reactive than ferrate(VI).

From the kinetic perspective, the reactivity of ferrate(VI) with organic pollutants is described as second-order with the second-order rate constants from 3.0×10^{-2} to 1.7×10^{7} 1/(M s) (see Table 8.1). Only in the case of an excess of ferrate or pollutants, the system behaves as the first-order. In this special case, the apparent second-order rate constant is often examined as a function of pH (Sharma 2013). The reactivity with the pollutants (X) can be described by several pathways. The first possibility is reduction of Fe(VI) to Fe(V) by electron transfer with formation of radical (Eq. 8.7). Another pathway is that the two-electron transfer creates radicals (Eq. 8.8) or dimer (Eq. 8.9). The formed radical species react with ferrates (Eq. 8.10). Finally, oxygen atom transfer can be observed (Eq. 8.11). This pathway was confirmed for instance for aniline forming Fe(IV) and phenylhydroxylamine. Consequently, reactions involving the described products (Eqs. 8.7, 8.8, 8.9, 8.10 and 8.11) are initiated and influenced by the inherent structure of each pollutant. In addition, self-decomposition of ferrate can take place, leading to the formation of Fe (IV), Fe(V), and reactive oxygen species as $O_2^{\bullet -}$ and H_2O_2. The reactive oxygen species can participate in the reaction with pollutants.

$$\mathrm{Fe(VI)} + \mathrm{X} \rightarrow \mathrm{Fe(V)} + \mathrm{X} \tag{8.7}$$

$$\mathrm{Fe(VI)} + \mathrm{X} \rightarrow \mathrm{Fe(IV)} + 2\mathrm{X} \tag{8.8}$$

$$\mathrm{Fe(VI)} + \mathrm{X} \rightarrow \mathrm{Fe(IV)} + \mathrm{X}_2 \tag{8.9}$$

$$\mathrm{Fe(VI)} + \mathrm{X} \rightarrow \mathrm{Fe(IV)/Fe(V)} + \text{product X} \tag{8.10}$$

$$\mathrm{Fe(VI)} + \mathrm{X} \rightarrow \mathrm{Fe(IV)} + \mathrm{XO} \tag{8.11}$$

The reactions can be influenced by various parameters. One of the most important one is pH. A large number of organic pollutants react rapidly with ferrates under neutral or slightly acidic pH, for example, substituted anilines, tetrabromobisphenol A, atrazine and more (Han et al. 2018; Sun et al. 2018; Zajíček et al. 2015). This is caused by the presence of $HFeO_4^{2-}$, which is a preferable species

Table 8.1 Selected organic pollutants and rate constants for reaction with ferrate (Adapted from Rai et al. 2018)

Organic pollutant	pH	Rate constant *k* (1/M s)
Hydroquinone	9.0	2.0×10^5
Cysteine	12.4	7.6×10^2
2-mercaptoethanesulfonic acid	9.0	3.0×10^4
2-mercaptobenzoic acid	10.0	2.5×10^4
3-mercaptopropionic acid	9.0	1.3×10^4
Methyl hydrazine	9.0	9.8×10^3
Aniline	9.0	6.2×10^3
p-toluidine	9.0	1.3×10^3
p-aminobenzoic acid	9.0	4.3×10^1
p-nitroaniline	9.0	3.0×10^1
Thiourea	9.0	3.4×10^3
Benzenesulfinate	9.0	1.4×10^2
Methionine	9.0	1.3×10^2
Cystine	12.4	1.2×10^2
Glycine	8.0	1.0×10^2
Trioxane	9.0	5.8×10^1
Glyoxylic acid	8.0	7×10^2
Dimethylamine	8.0	2.0×10^2
Iminodiacetic acid	8.0	1.0×10^2
Diethylsulfide	8.0	1.0×10^2
Thiodiethanol	8.0	1.0×10^2
Phenol	9.0	8.0×10^1
Nitriloacetic acid	8.0	2.0×10^0
N-methyliminodiacetic acid	8.0	2.0×10^0
Dimethylsulfoxide	8.0	1.0×10^0
Diethylamine	8.0	7.0×10^{-1}
Formaldehyde	8.0	5.0×10^{-1}
Acetaldehyde	8.0	4.0×10^{-1}
Glycolic acid	8.0	4.0×10^{-1}
Oxalic acid	8.0	1.0×10^{-1}
Ethyl alcohol	8.0	8.0×10^{-2}
Isopropyl alcohol	8.0	6.0×10^{-2}
Methyl alcohol	8.0	3.0×10^{-2}
4-methylphenol	7.0	6.9×10^2
Estradiol	7.0	7.7×10^2
Bisphenol A	7.0	6.4×10^2
Phenol	7.0	7.7×10^1
Octylphenol	9.1	1.8×10^3
Buten-3-ol	7.0	1.2×10^1
Ibuprofen	9.0	4.0×10^{-1}
Carbamazepine	8.0	1.6×10^1
Benzophenone-3	8.0	3.4×10^2

(continued)

Table 8.1 (continued)

Organic pollutant	pH	Rate constant *k* (1/M s)
Triclosan	7.0	4.1×10^2
Ciprofloxacin	7.0	4.7×10^2
Ciprofloxacin	8.0	1.1×10^2
Sulfamethizole	7.0	1.3×10^3
Sulfamethoxazole	7.0	1.3×10^3
Tetracycline	7.0	3.0×10^2

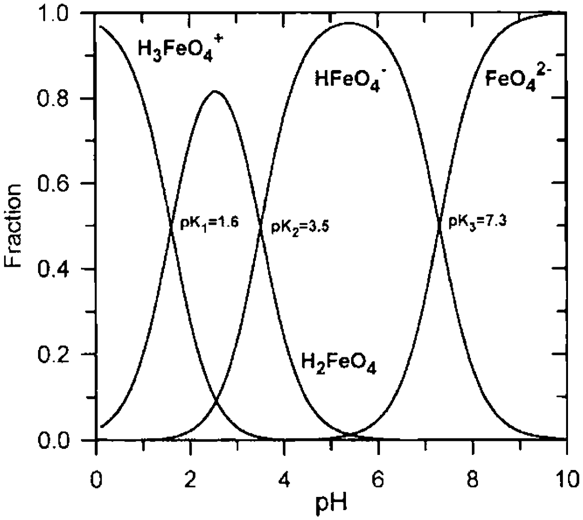


Fig. 8.5 Ferrate species under different pH (Adapted from Sharma 2013)

of ferrate under pH ranging from 4 to 7 (Fig. 8.5). This protonated species exhibits higher oxidation strength because it has larger spin density on oxo-ligands as an unprotonated counterpart. This was investigated by density functional theory (DFT) calculations (Kamachi et al. 2005). On the other hand, the rate constant of another organic pollutants can be limited by acidic pH. For example, this was observed for glycine and serine (Noorhasan et al. 2010). Another example can be phenol with optimal pH 9 for reaction with ferrate. A pH value in combination with reaction ratios can also influence the formation of reaction products. It was observed that oxidation of hydrogen sulfate by ferrate(VI) at pH 7 provided only thiosulfate as the final product; however, at higher pH and higher stoichiometric ratios, sulfite and sulfate were formed as well (Sharma 2002).

Numerous reactions of ferrate(VI) with various aliphatic and aromatic organic compounds were published (Table 8.1) (Rai et al. 2018). Ferrate easily reacts with electron-rich organic moieties such as olefins, amines, phenols, anilines, etc. In addition, adsorption on precipitating reaction products of ferrate can occur. The reactivity of ferrate was investigated by not only simple hydrocarbons, phenol, or chlorinated ethylenes but also complex organic pollutants with a more complicated structure. Contamination of drinking water sources with micropollutants, contamination of surface water with runoffs, and contamination of wastewaters with effluents from industry or less efficient wastewater treatment plants represent rather varied occurrence of pollutants, which can be potentially treated by ferrates.

One of the most discussed groups of pollutants occurring in surface- and wastewater is estrogens. The reactivity of ferrates with estrogens was tested and, except for ferrate(IV), an efficient removal/degradation of estrogens was observed (Machalová Šišková et al. 2016). The intermediates confirmed oxidation steps in the degradation. The hydroxyl groups of the parent molecule were attacked by the ferrate, which led to quinone-like structures, and subsequently the opening of an aromatic ring was observed. The product of degradation was malonic acid, finally mineralized to water and carbon dioxide (Fig. 8.6).

Another abundantly occurring pollutants are pesticides and herbicides. Most of them constitute a threat to the environment due to endocrine disrupting properties and bioaccumulation. As an example of this pollutant family, total atrazine and iodosulfuron degradation can be mentioned. Although the kinetics of the reaction was fast, some of the intermediates were determined (Zajíček et al. 2015). The oxidation of alkyl chain by ferrate(VI) generated a carbonyl group in structure of the intermediate phase. Ferrate predominantly attacks the ethyl group rather than the isopropyl group in the pollutant structure (Fig. 8.7). Generally, the formation of molecules with higher molar mass (oxygen insertion into the structure) is relatively common. This was, for instance, observed also during carbamazepine oxidation (Hu et al. 2009). For iodosulfuron degradation, products formed from the fission of the parent molecule (the both S-N and C-N bond cleavage) were confirmed.

In addition to carbamazepine or estrogens, lots of different pharmaceutical compounds constitute a threat to the purity of water and for the environment. Long-term exposition can cause toxic effects; and in the case of antibiotics, related increasing bacterial resistance was observed. The commonly discussed point is that these compounds are not fully removed from water in wastewater treatment plants. Ferrate(VI) exhibited effective oxidation properties to pharmaceuticals such as ciprofloxacin, enrofloxacin, sulfamethoxazole, ibuprofen, trimethoprim, propranolol, flurbiprofen. For most of them, optimal pH range was at neutral or slightly basic, which is acceptable for water treatment and does not increase operational costs. As another example of pharmaceuticals degradation, breaking of isoxazole ring was observed for sulfamethoxazole and conversion of amino group to nitro group or nitroso group. The determined final products were thus less toxic than the parent compound (Sharma et al. 2006).

Fe(VI) was also identified as an efficient oxidant to remediate several antibiotics such as β-lactam (cloxacillin, ampicillin, amoxicillin, penicillin G, cephalosporin) with the attack on the thioether moiety, tetracycline, and fluoroquinolone (Feng et al. 2016, 2017; Sharma et al. 2013, 2016a). Penicillin G and cephalosporin were converted initially to sulfoxide derivatives and finally to sulfones. Moreover, in the case of cephalosporin, also C-N bond can be attacked by a ferrate(VI) ion to form ammonia (Sharma 2010; Sharma et al. 2013). During the degradation of aliphatic amines by Fe(VI), dealkylation products or respective hydroxylamines are formed,

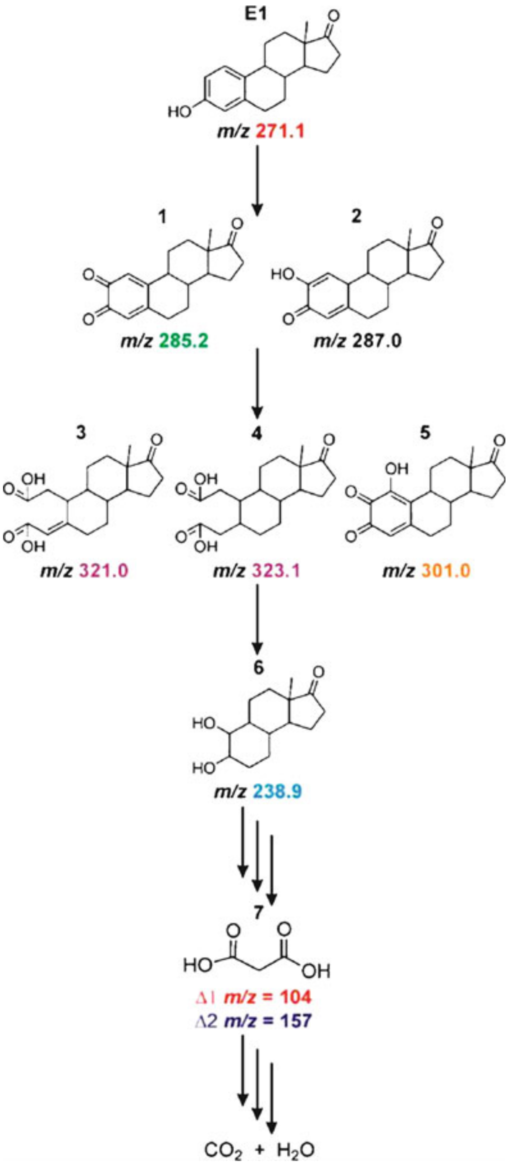


Fig. 8.6 Degradation of estrone by ferrate (VI) (Adapted from Machalová Šišková et al. 2016)

e.g., in the case of propranolol, ciprofloxacin, metoprolol, tramadol, atenolol (Rai et al. 2018). In the case of β-blockers, due to their different structure, different reaction pathways are observed. Generally, initial cleavage of an aromatic ring was observed. Carbonyl products were formed with subsequent transformation to a hydroxylamine derivative after the attack of ferrate on the amine moiety (Sharma et al. 2016a). Some analgesics react with ferrate(VI) very slowly. In case of tramadol, estimated degradation half-time is several minutes. Initially, ferrate reacts

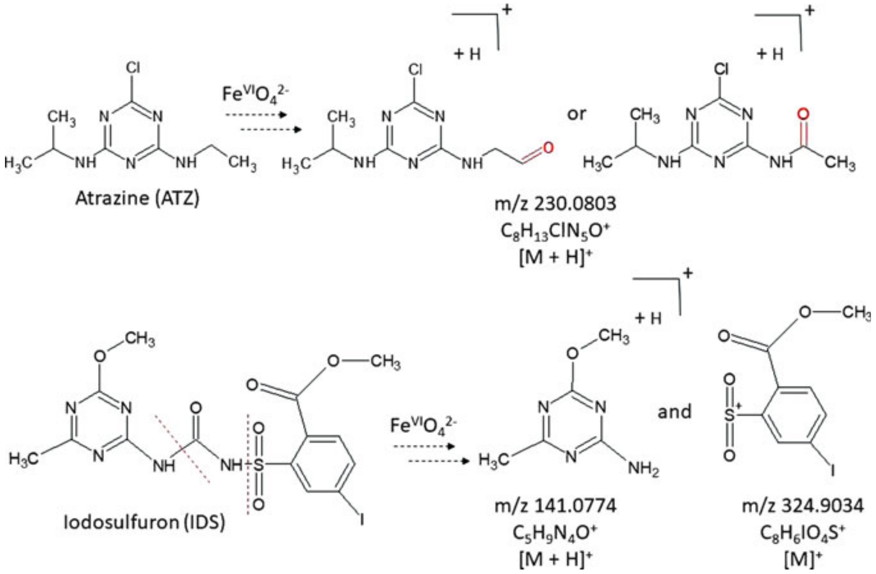


Fig. 8.7 Mechanism of atrazine and iodosulfuron degradation by ferrate(VI) (Adapted from Zajíček et al. 2015)

with amine group of tramadol with subsequent dealkylation yielding aldehyde and/or carboxylic groups (Sharma et al. 2016a).

Reactions of ferrate(VI) with sulfur- and nitrogen-containing pharmaceuticals are completed in a couple of seconds or minutes and the detected products are less toxic than the parent compounds (Sharma 2010). However, the related mechanism for the degradation is ambiguous and can hardly be elucidated empirically due to the rapid oxidation process and unstable intermediates for experimental trapping (Yu et al. 2017). In the case of sulfamethoxazole, DFT calculations were included in order to elucidate how ferrate(VI) initiated oxidative degradation process and to understand the reaction mechanisms (Yu et al. 2017). According to DFT study in the case of sulfamethoxazole, ferrate provides, at the initial step, oxygen atoms for the oxidation of aniline and isoxazole moieties. These theoretical findings are partially, not fully, supported by the experimental results (Casbeer et al. 2013; Hightower et al. 2012). The DFT calculations also show that a nucleophilic attack is a favorable pathway for ferrate(VI) to initiate oxidation of sulfamethoxazole, which has not been proposed previously. From the previous comments, it is clear that the degradation mechanism of micropollutants is very complicated and several oxidation products are formed during oxidation by ferrate.

Probably, the main problem is that the oxidation of drugs by ferrate(VI) can occur by several possible pathways (Sharma 2013). It is well known that several oxidation steps probably occur during the oxidation of a micropollutant by Fe(VI), which usually includes one- or two-electron transfer of Fe(VI) to form Fe(V) and Fe(IV), respectively, with Fe(II) and Fe(III) species as the final products. There is also a high probability of consecutive reactions of Fe(V) and Fe(IV), respectively, with other (micro)pollutants in the system; self-decompositions of all Fe(VI), Fe(V), and Fe (IV) species; reactions between all iron species from iron(VI) to iron(II) and/or oxygen species (i.e., H_2O_2) formed from either self-decompositions or during oxidation reaction of Fe(VI) with micropollutants (Sharma et al. 2015). Moreover, radicals of oxidized compounds formed during the degradation reaction can further react with mother compounds, with Fe(VI), Fe(V), Fe(IV), or with other radicals from different substances etc.

Dyes, hardly biodegradable (in)organic substances, can be also present in wastewaters (Lubello and Gori 2004). They can have toxic, carcinogenic, teratogenic, and mutagenic properties, some of them inhibiting the photosynthesis and biochemical pathways of aquatic animals and plants (Rai et al. 2018). Ferrate(VI) has been found to have great potential for their effective degradation. During the oxidation process, less toxic products are formed (Barışçı et al. 2016).

8.8 Removal of Heavy Metals and Metalloids by Ferrates

Heavy metals associated with exposure of highly toxic compounds of lead, cadmium, chromium, mercury, arsenic and others represent a severe threat to human health. Though toxicity and negative health effects of heavy metals have long been recognized, metals are widely used in a range of products including household appliances, paints, agriculture, motor vehicles, and electrical components. Contamination of all water types represents a growing danger in many countries all over the world because of the severe impact of such compounds on the population’s health. For example, Bangladesh, some parts of India, Nepal, and Vietnam are countries where arsenic and heavy metals contamination of surface and drinking water is particularly large, showing an upsurge of poisoning cases and, overall, an increased life-risk for a large fraction of human and animal populations. Apart from contamination of toxic metals, phosphates often enter the environment. The presence of high levels of phosphorus input into water causes eutrophication that adversely affects aquatic ecosystems and water quality. The specific effects of excess phosphorus include blooms of harmful algae that can release toxins, create dead zones (or hypoxia in water), cause fish death, and foul taste and odor of drinking water (Faridmarandi and Naja 2014; Järup 2003).

For efficient removal of metal ions, the remediation process should combine the properties of an oxidant, high adsorption capacity (with the low sorbent/metal ion ratio), and it should also enable at least partial incorporation of metal ion into the structure of the reaction products, thus preventing the metal(loid) leaching back to water. The ferrates can meet all the mentioned criteria and can act as a highly efficient constituent in various water treatment technologies.

Several studies have explored the use of ferrate(VI) for removal of inorganic pollutants, in particular toxic heavy metals from various water samples (Table 8.2). The removal efficiency can reach, in the case of some heavy metals (Zn, Cu, Mn), almost 100% (Rai et al. 2018). Fe(VI) has the greatest potential to remove also other

Table 8.2 Removal of inorganic pollutants by ferrate(VI)

Pollutant	Effective ratio	Solution	Reference
PO_4^{3-}	~3:1 (mass)	Micropollutants	Lee et al. (2009)
Radionuclides	1000:1 (molar)	Hard fresh water/ seawater	Petrov et al. (2016)
I^-	1:1 (molar)	DI water	Kralchevska et al. (2016b)
Sb^{3+}	~7.7:1 (mass)	DI water	Lan et al. (2016)
$Cd(CN)_4^{2-}$/Ni $(CN)_4^{2-}$	4:1 (mass)	DI water	Yngard et al. (2008)

DI deionized

metal ions, such as As(III), Pb(II), Cr(III), or Hg(II) via co-precipitation and/or oxidation (Jiang et al. 2006). Moreover, ferrate(VI) has proven its ability to remove some natural or artificial radionuclides (^{238}U, ^{226}Ra, ^{232}Th, ^{137}Cs, ^{90}Sr, ^{239}Pu, etc.) from various environmental samples (mines, waters) by their sorption in aqueous environment with concomitant co-precipitation with iron(III) oxy-hydroxy species followed by sedimentation. Interestingly, potassium ferrate effectively acted as a scavenger to remove a mixture of alpha- and beta-emitting radionuclides (^{137}Cs(I), ^{90}Sr(II), ^{152}Eu(III), ^{243}Am(III), ^{239}Pu(IV), ^{237}Np(V), ^{239}Np(V), and $^{238+233}$U(VI)) from water samples under laboratory conditions (Petrov et al. 2016; Rai et al. 2018).

Considering the high toxicity of arsenic compounds, many studies focused on their removal by ferrates (Jain et al. 2009; Lee et al. 2003). For instance Prucek et al. (2013) explained kinetics and mechanisms of arsenite and arsenate removing by ferrate(VI) (Fig. 8.8). A well-known fact is that sorption of metal ions is dependent on the pH value. This effect is connected with speciation of ions and surface charge. In the case of arsenic, decreasing the pH value sharply improved efficiency of arsenic removal. In these experiments, the sorption kinetics of arsenic removal was very fast and sorption equilibrium was reached approximately within 2 min. Ferrate (VI) removed almost all arsenic at an Fe/As weight ratio of 2/1 (at pH 6.6). The very important conclusion is that ferrate(VI) has the same efficiency in arsenite and arsenate removals. This is due to strong oxidizing properties of ferrate(VI) that oxidized arsenite to arsenate. The oxidation of arsenite was confirmed using X-ray photoelectron spectroscopy—XPS (Fig. 8.8d). On the basis of XPS results (i.e., As 3d high resolution spectra), only As(V) was detected. Therefore, arsenite can be effectively removed from water by ferrate(VI) even though this form of arsenic is difficult to remove from water by other processes. The combination of XPS and Mössbauer spectroscopy enables to reveal the mechanisms of As removal, which include two crucial aspects. Arsenic is partially incorporated into the crystal structure of solid precipitate of iron(III), which leads to an increase in the removal efficiency. Thus, arsenic is strongly bound to sorbent and is partially protected against leaching back into the environment. The remaining arsenic is adsorbed onto the surface of iron(III) oxide nanoparticles. Additionally, most of the formed phases are magnetically active; they can be separated easily from the medium by the application of an external magnetic field.

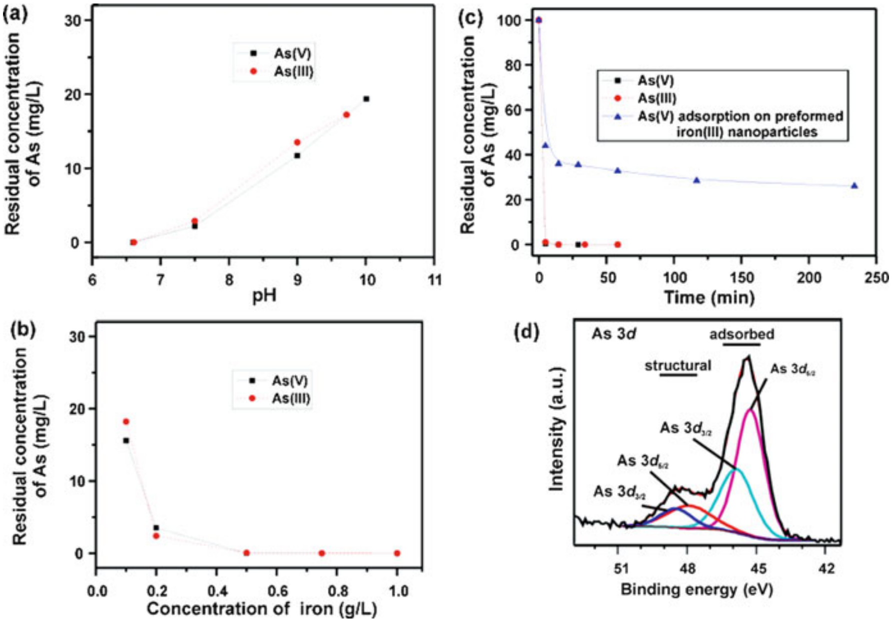


Fig. 8.8 Removal of arsenic by ferrate(VI). (**a**) Dependences of residual arsenic concentrations on the pH value of the reaction mixture (initial conditions: As = 0.1 g/L; Fe = 0.5 g/L); (**b**) dependences of residual arsenic concentrations on the concentration of iron (initial conditions: As = 0.1 g/L; the used pH = 6.6); (**c**) kinetics of arsenites and arsenates removal (initial conditions: As = 0.1 g/L; Fe = 0.5 g/L; and pH = 6.6); and (**d**) high-resolution As 3d core level photoelectron spectra of arsenate removal by ferrate(VI) sample. (Adapted from Prucek et al. 2013)

Further, removal of a wide range of heavy metals by ferrate(VI) has been studied. A thorough study by Prucek et al. (2015) showed that metal ions, such as Cd(II), Ni (II), Co(II), Cu(II), and Al(III), can be removed from water very effectively (Fig. 8.9). At an Fe/metal ion weight ratio of 1/0 or less, complete removal of Co (II), Cu(II), and Al(III) ions was observed. The ratio of 2/0 was required to remove Ni(II) ions completely from water. In the case of Cd(II) ions, the removal was ~70% even at an Fe/Cd(II) weight ratio of 15/1. These results were obtained at neutral or slightly acidic pH values. An increase in the pH enhanced the removal efficiency of heavy metal ions, whereas the removal efficiency of Al(III) decreased with increasing pH, which can be explained in terms of a more pronounced transformation of Al (III) ions to soluble $Al(OH)_4$. The mechanisms of metal ions removal were confirmed by the combination of XPS and Mössbauer spectroscopy techniques. The removal mechanism includes different processes for each particular metal. In the case of copper, cobalt, and nickel, ions are readily removed predominantly through the simultaneous formation of particular metal ferrite and γ-Fe_2O_3/γ-FeOOH core/shell nanoparticles embedding a part of heavy metals in their crystal lattice (i.e., octahedral sites); only a minor part of these elements is adsorbed on the surfaces of γ-Fe_2O_3/γ-FeOOH core/shell nanoparticles. Aluminum is partially incorporated in

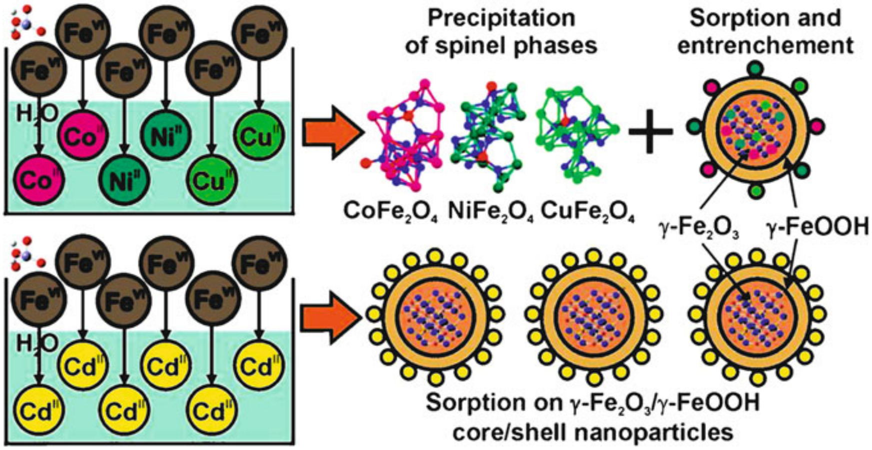


Fig. 8.9 The schematic illustration mechanisms of heavy metals removal by ferrate(VI). (Prucek et al. 2015, Copyright (2015) American Chemical Society)

the tetrahedral positions of the γ-Fe_2O_3 lattice and some portion of Al is adsorbed. Finally, cadmium would be treated by ferrate(VI) just at high Fe dosages with the predominant sorption. Therefore, there are three crucial aspects of the application of ferrate(VI) to the removal of heavy metals including: (i) the formation of metal ferrites ($CuFe_2O_4$, $CoFe_2O_4$, and $NiFe_2O_4$); (ii) structural incorporation of heavy metal ions into the crystal lattice of iron(III) oxide nanoparticles; (iii) the fast kinetic of metal removal even at very low ferrate(VI) dosages.

Similar results were achieved when ferrate(VI) was applied to metal cyanides, namely $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, $K_2[Ni(CN)_4]$, and $K_3[Cu(CN)_4]$. In this case, toxic cyanides are degraded by oxidation and simultaneously the metals ions are adsorbed from water on the surface of precipitated iron(III). (Filip et al. 2011; Yngard et al. 2008)

Several studies described the critical influence of phosphates ions on the sorption of metals ions from the aquatic environment. The mechanism of interaction of phosphates, when over-concentrated in drinking water, with ferrate(VI) and the efficiency in phosphate removal was studied by Kralchevska et al. (2016a). From the kinetic data of phosphate elimination (Fig. 8.10) a fast reaction of ferrate (VI) (within 2 min) depending on pH values is evident. The effect of pH is similar to the case of arsenic removal. When the pH decreases, the phosphate removal efficiency increases. This study showed that removal of phosphates by ferrate (VI) from water can be achieved efficiently at a low Fe/P mass ratio of 5/1 at pH ~7.0. Moreover, it is evident from the experimental data (mainly low-temperature/in-field Mössbauer spectra, Fig. 8.10d–f) that phosphates, treated by ferrate(VI), solely adsorb onto the surface of iron(III) oxide/oxyhydroxide nanoparticles formed from ferrate(VI). The observed extent of leaching (or desorption) of phosphate from the solid phase(s) is low. This mechanism is explained on the basis of the comparison of

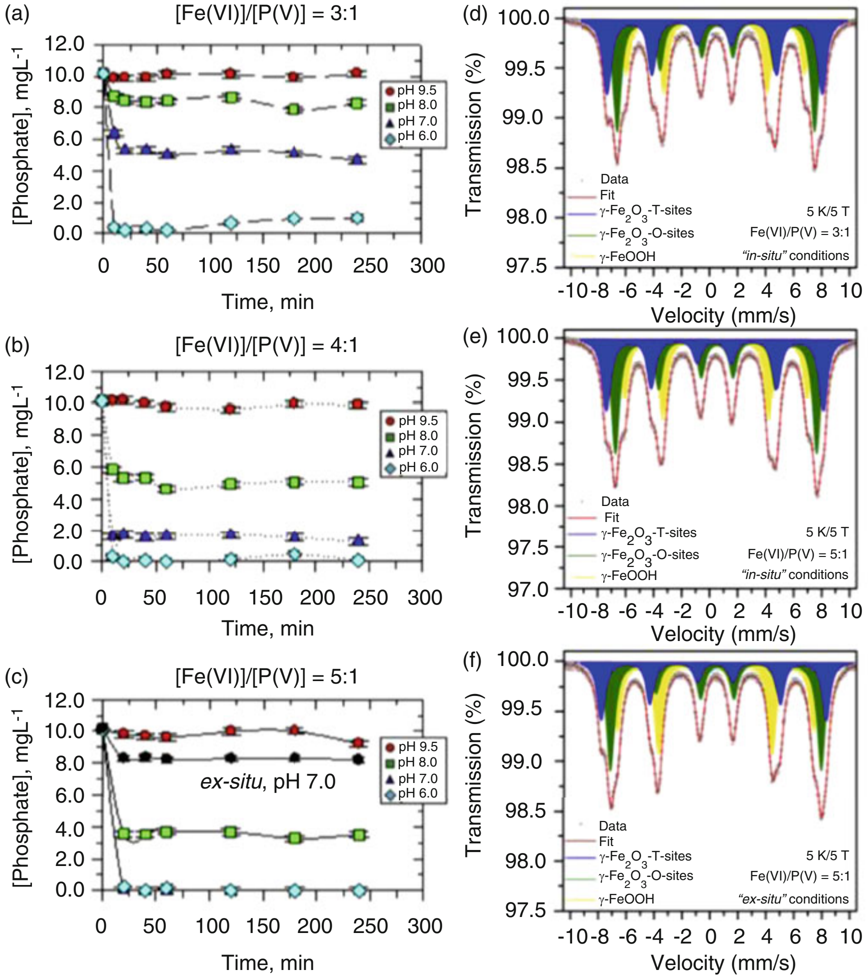


Fig. 8.10 Residual phosphate concentrations as a function of the reaction time and pH of the reaction mixture at Fe/P mass ratio of (**a**) 3/1, (**b**) 4/1, and (**c**) 5/1. (**d–f**) In-field (5 T) low-temperature (5 K) ^{57}Fe Mössbauer spectra of variously treated phosphate (Fe/P = 3/1, 5/1 and at pH ~7.0 for sorption on preformed iron oxides). (Adapted from Kralchevska et al. 2016a)

ferrate-treated phosphate with phosphate sorption on preformed iron(III) oxide/ oxyhydroxide nanoparticles.

The efficiency and mechanism of heavy metals and arsenic removal by ferrate (VI) is dependent on the chemistry of the real water. Therefore, Kolařík et al. (2018) focused on the description of the influence of commonly present inorganic ions and organic carbon in waters on metal removal by ferrate(VI). Ions such as chlorides, nitrates, carbonates, and sulfates as well as humic acid had marginal or no effect on the efficiency in removing arsenates by ferrate(VI) (Fig. 8.11). By contrast, the

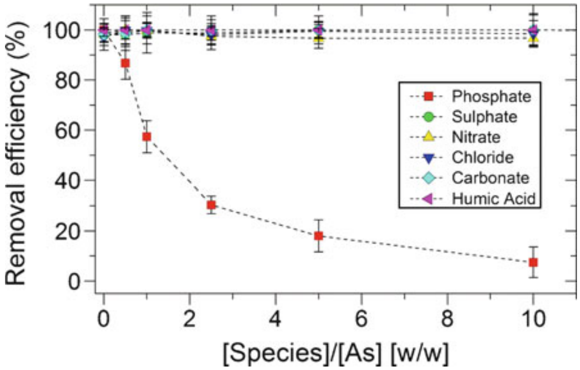


Fig. 8.11 Effect of concentrations of particular ions and humic acid on removal of arsenates by ferrate(VI) (initial conditions: As = 10 mg/L, Fe = 30 mg/L, pH = 6.6, and time = 24 h). (Adapted from Kolařík et al. 2018)

presence of phosphates ions had a negative influence on the efficiency in arsenates removal by ferrate(VI). With the increased concentration of phosphates, the efficiency in arsenates removal was found to decrease. The three crucial aspects of phosphates concerning the arsenate removal mechanism have been identified: (i) At a low P/As weight ratio (up to 1/1), the incorporation of arsenates ions into the crystal structure of the γ-Fe_2O_3 nanoparticles was suppressed. Arsenates were mainly adsorbed on the surface of γ-Fe_2O_3/γ-FeOOH nanoparticles. (ii) Increasing the P/As weight ratio (more than 1/1) led to the competition between arsenates and phosphates sorption on the surface of γ-Fe_2O_3/γ-FeOOH nanoparticles. With increased concentration of phosphates ions, the arsenates amount on the surface of γ-Fe_2O_3/γ-FeOOH nanoparticles was reduced. (iii) Further increase in the phosphates concentration, the complexation of iron(III) ions with phosphates ions occurred, which led to the reduction of arsenates removal efficiency due to a lower content of precipitated γ-Fe_2O_3/γ-FeOOH nanoparticles. In real waters, the arsenic contamination is usually present with phosphates, it is therefore necessary to know the content of phosphates in arsenic contaminated waters for its effective elimination.

8.9 Disinfection Properties of Ferrates

The ability of biological processes such as nitrification and denitrification to eliminate the resistant types of bacteria is typically limited or minimal (Kümmerer 2009). Chemical disinfection using chlorine is one of the easiest and the most frequent means for water treatment. However it can, on one hand, remove microorganisms and micropollutants from water but, on the other hand, harmful or hazardous by-products are formed during this process (Rai et al. 2018). To overcome this problem, other treatment processes and agents, e.g., ferrate(VI), are used/tested to eliminate microorganisms in water. During the water treatment by Fe(VI), no mutagenic and carcinogenic by-products are produced as demonstrated by Ames test (Jiang 2014; Jiang and Lloyd 2002; Rai et al. 2018). Ferrate(VI) can achieve very high (even 100%) efficiency in removing coliform bacteria from wastewaters due to its high oxidation potential at relatively low dosage (Jiang and Lloyd 2002; Kubiňáková et al. 2017; Rai et al. 2018).

Disinfection properties of ferrate were tested on various germs (*Bacillus cereus*, *Streptococcus bovis*, *Staphylococcus aureus*, *Shigella flexneri*, *Enterococcus faecalis,* and *Salmonella typhimurium*) and virus coliphage f2 (*Picornaviridae*) (Rai et al. 2018; Kubiňáková et al. 2017; Birošová et al. 2014; Sharma et al. 2015). This virus is usually present in sewage water and is highly resistant to chlorination (Kazama 1995). The algae caused a growing problem not only in cooling water but also in the production of drinking water. Algae removal from water is difficult because of their small size and the low specific gravity. Alga *Cladophora aegagropila* has been effectively eliminated by electrochemically synthetized potassium ferrate. The mechanism of action of Fe(VI) on the cells of algae can be evaluated by microscopic examination. Any apparent damage to the cell wall proved that ferrate(VI) penetrated into the cell and subsequently caused damage to internal organelles (Kubiňáková et al. 2017).

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