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Application of Ferrate for Advanced Water and Wastewater Treatment

Ansaf V. Karim, Sukanya Krishnan, Lakshmi Pisharody and Milan Malhotra

Abstract

Treatment of recalcitrant organics and inorganics present in wastewater is a major challenge. Conventional biological treatments alone are not capable of removing these toxic compounds from wastewater. To overcome these problems, advanced oxidation processes (AOPs) have been used to completely mineralize or transform the organics into simpler compounds, which can then be treated through biological processes. However, conventional AOPs result in the generation of byproducts, which are known to have higher toxicity. Among various AOPs, ferrate has been gaining popularity because of its advantages such as high oxidation potential, no byproduct formation and also non-toxic end products. The end product generated also acts as a coagulant, which thereby enhances the removal efficiency. In the present chapter, the chemical properties, preparation methods and the factors affecting the stability of ferrate were evaluated based on literature. Further, ferrate oxidation as a potential method for the treatment of both organic and inorganic pollutants in drinking and real wastewater is discussed.

Keywords: ferrate, oxidation process, disinfection, iron chemistry, synthesis

1. Introduction

Scientific discoveries and development in pharmaceuticals, pesticides, personal care products (PCP) and basic sanitation have improved the lifestyle and living standards of humans across the globe. However, these developments come with an environmental cost. In recent past, environmental and human health risks associated with traces of pharmaceutical, pesticides and microplastics (from PCP) have been studied by various researchers. Due to the transformation and interaction of these compounds with the environment, they can enhance the resistance of microbes, thus making them resistant to antibiotics. Furthermore, some of the pesticides have been proven to have a carcinogenic effect. The microplastics generated from PCP have now been reported to be the part of the food chain mostly from sea salts and fish. With these environmental challenges, there has been a sharp increase in the research for the treatment and removal of these emerging contaminants.

Various research groups have used different physicochemical techniques such as adsorption, Fenton treatment, zero-valent iron, ultraviolet (UV)-catalytic,

electro-oxidation and wet oxidation [1–3] for the sustainable treatment of these contaminants. The techniques mentioned above have their advantages regarding their nonselective behaviour, high removal efficacy, and simpler byproducts. The higher cost associated with AOPs is a major limitation for field applicability.

From the past two decades, advanced oxidation processes (AOPs) have been gaining popularity for the treatment of water and wastewater contaminants. AOPs use hydrogen peroxide and ozone, among other chemicals that have high oxidation potential. These chemicals can oxidize organic molecules to simpler molecules and themselves get reduced. During AOPs, in situ hydroxyl radicals are formed, which

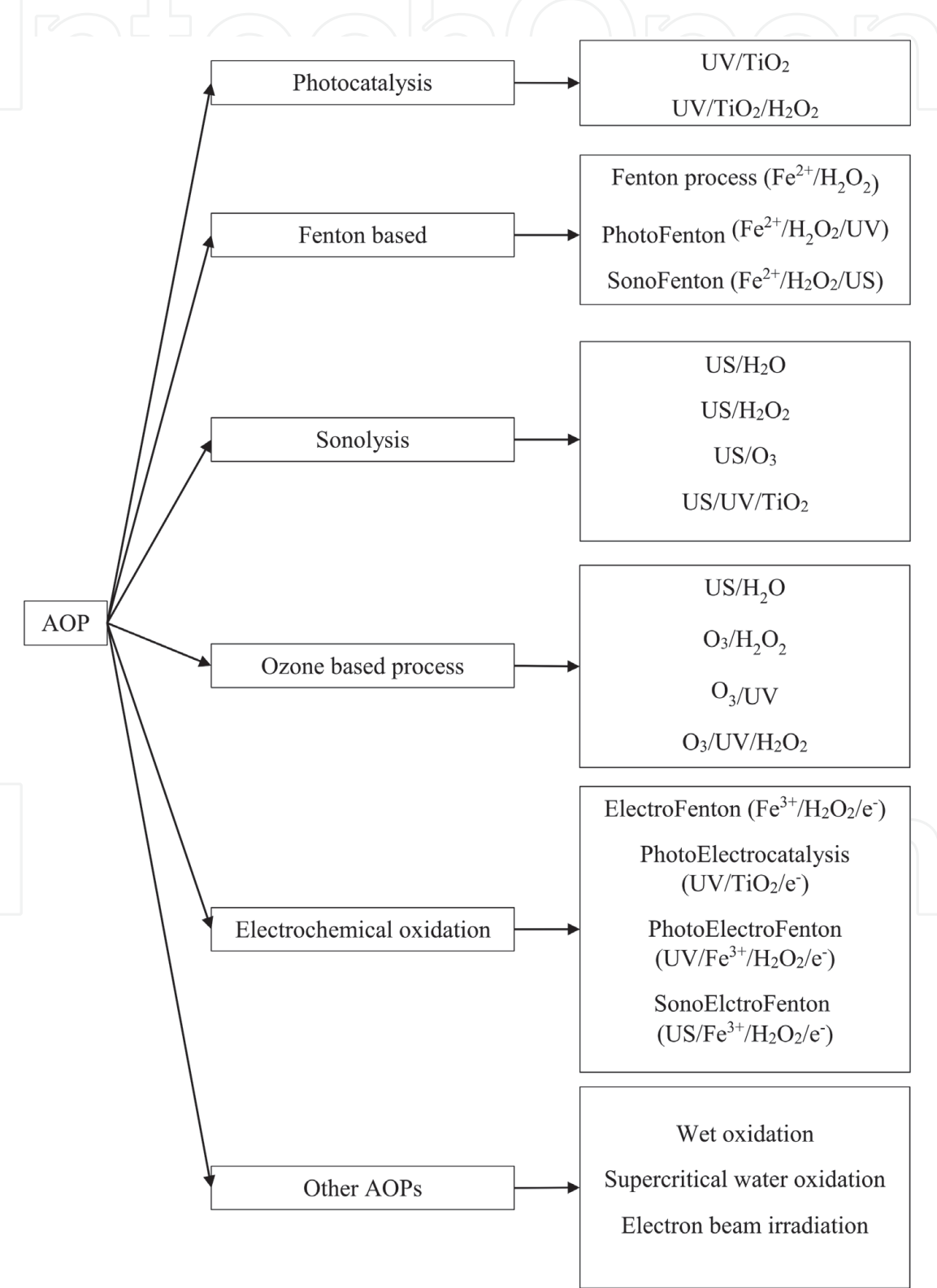


Figure 1.
Broad category of AOPs [4].

further reacts with organic molecules. The organic molecule may undergo various reactions such as partial cleavage, dechlorination, fragmentation or complete mineralization, depending on the chemical structure of molecule and reaction condition. The broad category of AOPs is shown in **Figure 1**.

Innovative technologies using alternative sources such as peroxides, ferrates, ozone, etc. can significantly improve the wastewater treatment due to their higher selectivity and efficiency. Among them, ferrate [Fe(VI)] is a promising choice for environmental remediation. It does not produce any harmful byproducts during treatment and provides efficient degradation of organic, inorganics and microorganisms over a wide range of pH. This chapter provides a detailed review of chemical properties, preparation methods and factors affecting the stability of ferrates. Further, the chapter also reviews the oxidation potential of ferrates for the environmental remediation and disinfection.

2. Chemical structure and stability of ferrate

Typically iron (Fe) exists in two oxidation states either as ferrous (Fe(II)) or ferric (Fe(III)). However, under strong oxidizing conditions, a higher oxidation state (i.e. +IV, +V and +VI) of iron can be achieved, which is referred to as a ferrate. Based on the pE-pH diagram, which is also known as Pourbaix diagram of iron (**Figure 2**), we can visualize the presence of various forms of iron at different pH and under oxidative/reductive environment. A reducing environment is represented by low pE values; high pE values represent an oxidizing environment. Ferrates are predominating in the top region of the pE-pH diagram, whereas iron exists as Fe (0) at the bottom.

Among the various higher oxidation state, the +VI state of iron is comparatively stable and easier to produce. The literatures, based on XRD of solid ferrate, proposed a tetrahedral structure of ferrate (**Figure 3**). In ferrate, centrally placed Fe⁺⁶ is covalently bonded to four equivalent oxygen atoms at the corner of the tetrahedron.

In the aqueous phase, there are many factors (such as pH, temperature and ferrate concentration) on which the stability of ferrate depends. Ferrate ions and water molecules reacts to form ferric oxide (Fe₂O₃), oxygen gas, and hydroxyl ions (Eq. (1)). Due to the release of hydroxyl ions, the resulting pH of the solution is highly alkaline. The ferric oxide generated as an end product acts as a coagulant:



Under the acidic environment, ferrate is quite unstable and rapidly undergoes exothermic degradation. In aqueous solution of pH ~5, the ferrate (1 mM) was reported to be completely degraded within 7 min [5]. The stability of ferrate tends to improve with an increase in pH, as can be seen in **Figure 4**. For pH ~10, the ferrate concentration remained almost constant. At pH of above 10, the stability of ferrate also tends to deteriorate. For a ferrate concentration of 0.25 mM and a pH of 12, reductions of ~ 60% were reported within 10 min [6].

A diluted ferrate solution is reported to be more stable than a concentrated solution. The critical ferrate concentration is 0.025 M; a ferrate concentration higher than this (0.025 M) in solution tends to degrade rapidly. When comparing the stability of ferrate at different concentrations, it was reported that ~89% of ferrate concentration remained as ferrate for 0.02 and 0.025 M strength for 1 h. However, complete degradation was reported for solution with a 0.03 M concentration in that specific duration [7].

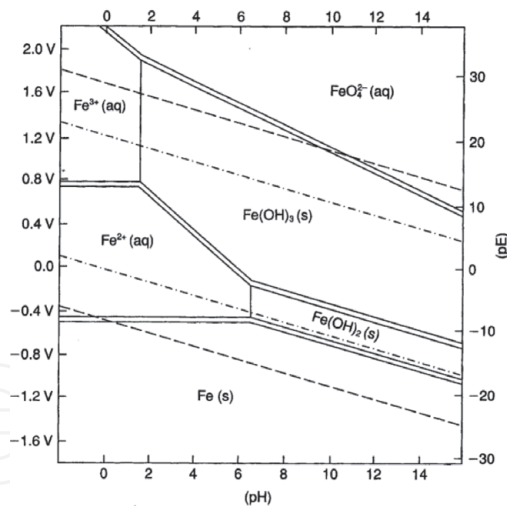


Figure 2.
Pourbaix diagram for iron (1 M) solution.

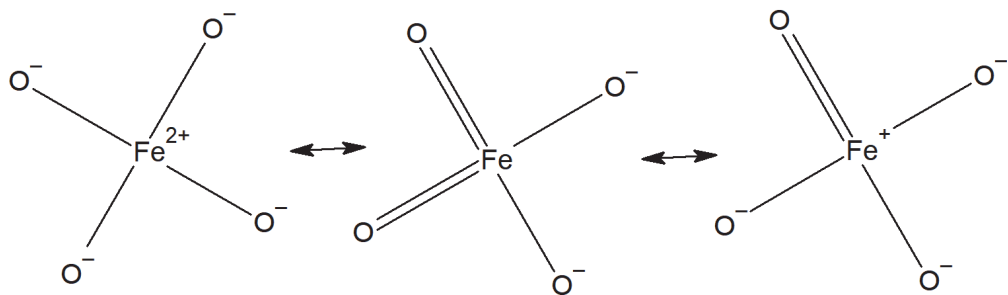


Figure 3.
Resonance hybrid structure of ferrate.

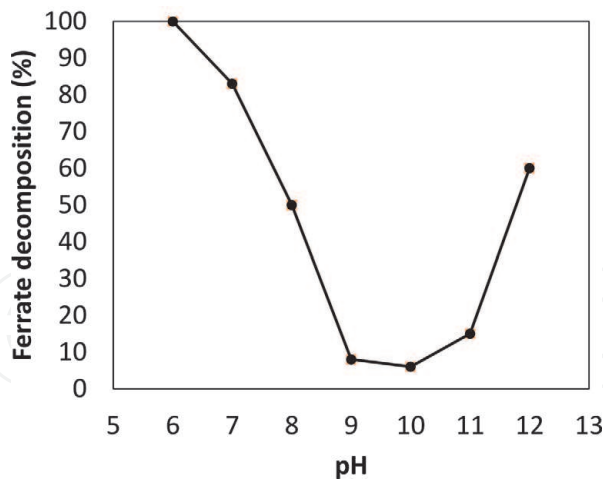


Figure 4.
Stability of ferrate in the aqueous phase at different pH [6].

Co-ions such as $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ in $100 \mu\text{M}$ concentration were reported to increase the decomposition rate of ferrate (2 mM). However, at lower concentration, the influence of co-ion ($0.1 \mu\text{M}$) on ferrate decomposition was reported to diminish. No significant influence of other ions ($\text{Ba}(\text{II})$, $\text{Ca}(\text{II})$, $\text{Fe}(\text{III})$, $\text{Mg}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Sr}(\text{II})$) and salts (KIO_4 , $\text{K}_2\text{O}_9\text{B}_4$, K_3PO_4 , Na_2WO_4 , Na_2MoO_4 , Na_2SiF_6) on ferrate degradation was reported [8].

The temperature of the aqueous phase can also influence the stability of ferrate. Ferrate solution (0.01 M) kept at 0.5°C was reported to remain stable

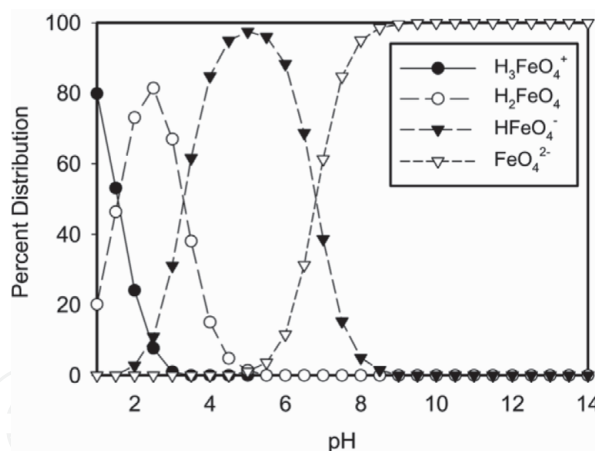
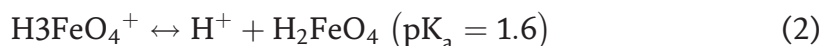


Figure 5.
Different species of ferrate in the aqueous phase [10].

(~2% reduction) even after 2 h. On the other hand, the ferrate concentration was found to be reduced by ~10% at a temperature of 25°C [9]. External factors such as light are not known to have any significant influence on the stability of ferrate (0.01 M) [9].

Depending on the pH of the solution, four different species of ferrate can exist, as shown in **Figure 5**. Initially, two unstable species of Fe(VI) (i.e. H₂FeO₄ and HFeO₄⁻) were reported in phosphate buffer (0.2 M solution). Three protonated species of Fe(VI) were reported in phosphate/acetate buffer (0.025). Based on pK_a values, it can be seen that in the alkaline environment, most of the ferrate exist as FeO₄²⁻. In neutral conditions, HFeO₄⁻ is the dominating species:

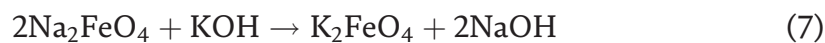
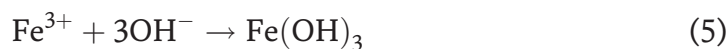


3. Synthesis of ferrate

3.1 Wet synthesis

The wet oxidation synthesis of ferrate involves oxidation of ferric to ferrate under high pH conditions. The solution containing ferrate obtained by this procedure is highly unstable, which thereby demands subsequent procedures of precipitation, washing and drying to obtain a stable solid product. Numerous methods have been tried to prepare a stable solid product containing ferrate(VI). However, the subsequent recovery of ferrate is difficult because of the increased solubility of Na₂FeO₄ in solution saturated with NaOH. The procedure involving the flow of chlorine gas through the ferric salt resulted in a solid product with 41.38% of Na₂FeO₄ [11, 12].

The method of production of ferrate by wet oxidation is known since the 1950s. The method involves a reaction between ferric chloride and sodium hypochlorite in the presence of an alkali such as sodium hydroxide. Further recovery of potassium ferrate is obtained by precipitation with potassium hydroxide. Even though a percentage recovery of potassium ferrate as high as 96% could be obtained, the maximum yield percentage obtained by continuous efforts was 75%. Earlier the recovery was poor as 10–15%. The basic reactions involved in the process are shown below [13, 14]:



3.2 Dry synthesis

The dry oxidation method for ferrate synthesis is a very old method. However, the method involves high risks as it can lead to an explosion at elevated temperature. Recent developments include synthesis of ferrate salt by calcination of a mixture of potassium peroxide and ferric oxide at a temperature ranging from 350 to 370°C. Another method involves oxidation of iron oxide with sodium peroxide at a temperature of 370°C, with a continuous flow of dry oxygen in a ratio of 4:1, yielding sodium ferrate. The product by this reaction results in a red-violet colored solution containing tetrahedral ion FeO_4^{2-} [11, 15, 16]. The % recovery of ferrate was not higher than 55% in this method [17]. The equation for the reaction is given below:

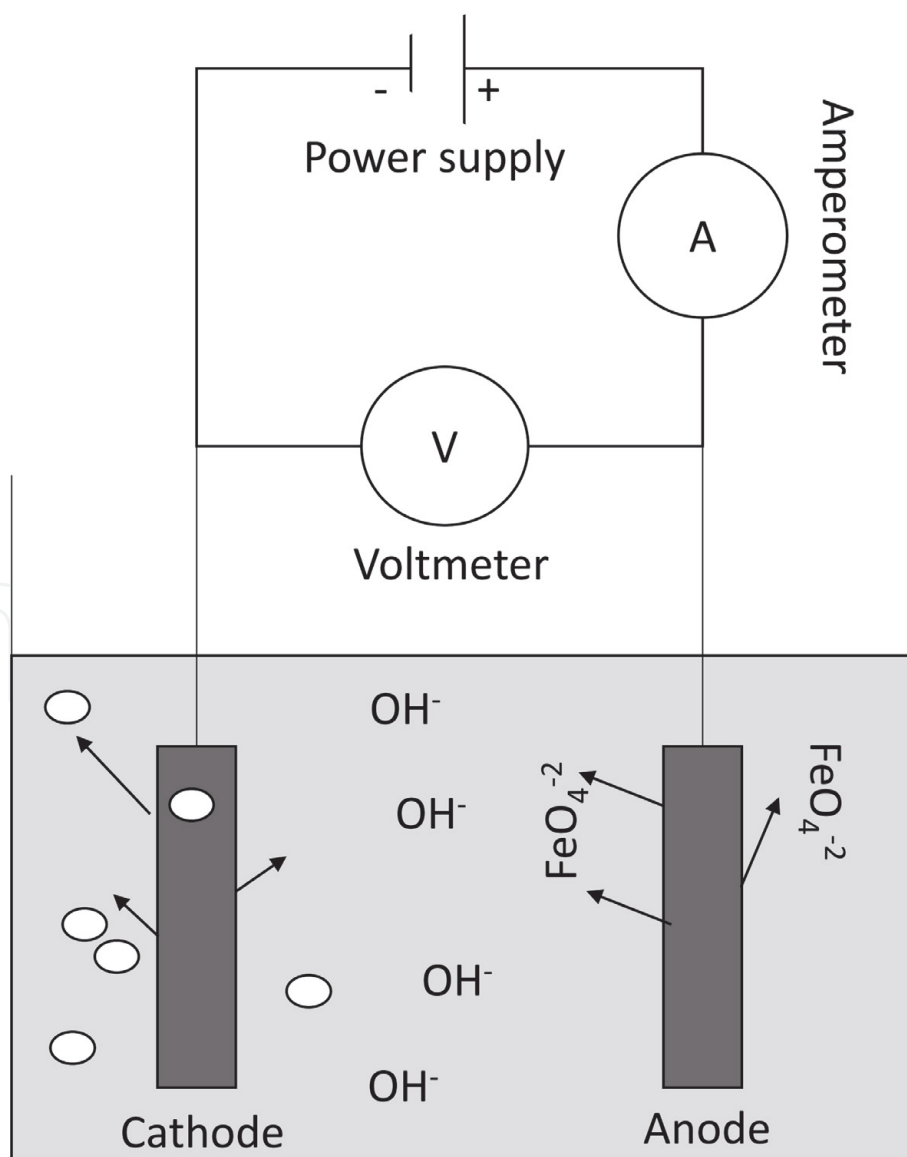
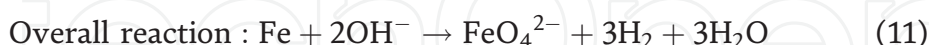
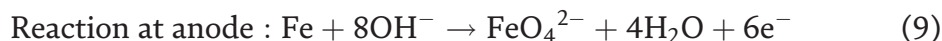


Figure 6.
Electrochemical cell for ferrate production [18].

3.3 Electrochemical synthesis

During the electrochemical synthesis of ferrate, anodic dissolution of iron takes place in a strongly alkaline solution. The current applied during the synthesis process oxidizes the iron to ferrate in the alkaline solution (KOH or NaOH) (**Figure 6**). The reactions at the anode and cathode are as follow:



Factors such as anode composition, current density and strength of electrolyte govern the production of ferrate. The major advantage of electrochemical synthesis is its simplicity and no costly chemical requirement.

4. Application of ferrate in environmental remediation

The increasing occurrence of emerging pollutants such as pharmaceuticals, dyes, heavy metals and endocrine disrupting compounds, among others, in wastewater has generated a growing concern. Due to the recalcitrant nature of these compounds, they remain in the environmental matrices for longer duration and are not degraded naturally or by biological reactions. Ferrate as an oxidizing agent is a promising choice for the remediation of water and wastewater containing recalcitrant pollutants. They are able to oxidize compounds in a shorter time period when compared to permanganate and chromate [19]. The degradation potential of ferrate for water and wastewater treatment mainly depends upon the pH, initial ferrate concentration, presence of coexisting ions and temperature [20]. They can be easily reduced to insoluble and non-toxic Fe(III) species and can adsorb organic compounds, resulting in its removal [21]. In addition to the higher oxidizing ability of Fe(VI), other intermediate oxidation states of iron Fe(V) and Fe(IV) are claimed to help oxidation of organic and inorganic compounds [19]. The following section describes the application of ferrate as an oxidant for remediation of various pollutants.

4.1 Phenolic compounds

The removal of phenolic compounds from environmental matrices has attained considerable attention in recent years due to its recalcitrant and hazardous properties. The oxidative removal of these types of compounds from water and wastewater using ferrates Fe(VI) has been extensively studied by the researchers these days. Chen et al. [22] have examined the removal of four different types of phenolic compounds, such as 2-benzylphenol, phenol, chlorophene and 4-chlorophenol by Fe(VI) at pH 8. It was observed that the presence of chlorine and benzyl groups helps in the increased reactivity of Fe(VI) with phenolic compounds, and the degradation was observed to be in the order of chlorophene > 4-chlorophenol > 2-benzylphenol > phenol. They established the complete degradation pathway and various intermediates formed by mainly four pathways, such as hydroxylation of the benzene ring, C—C bond cleavage, chlorine atom substitution by a hydroxyl group and single-electron coupling.

A similar study of Chen et al. [23] demonstrated almost complete degradation of polychlorinated diphenyl sulphides (PCDPSs) within a short period of time

(~240 s) at pH 8. Also, they established the pathway of degradation and toxicity potential of products, which suggests that PCDEPs' oxidations occur at the S(II) moiety by ferrates and form oxidation products that are non-toxic to aquatic organisms. pH is one of the critical factors for oxidation reactions which also affects the stability and oxidation potential of ferrate ion [6]. However, high alkaline pH of liquid ferrates imparts an adverse effect on disinfection treatment by the formation of harmful disinfection byproducts [24]. Hence, detailed research should be carried out for understanding the effect of pH in the treatment of various recalcitrant pollutants with different ferrate concentrations.

The study conducted by Zhang et al. [25] demonstrated the use of Fe(VI) for the removal of one of the most renowned endocrine disruptors, bisphenol-A, from water. They observed the complete degradation of BPA at Fe(VI)/BPA molar ratio of 3.0 and 1.5 mg L⁻¹ BPA initial concentration within 30 minutes of oxidation under weak acidic pH. In order to enhance the degradation of various recalcitrant compounds, various homogeneous reducing agents such as sodium thiosulfate (Na₂S₂O₃) and sodium sulphite (Na₂SO₃) have been used in recent years. In the recent study by Sun et al. [26], the application of heterogeneous carbon nanotube along with ferrates for enhanced degradation of bromophenols. The reaction kinetics was found to follow second-order over a wide range of pH (6-10). It was found that the coupling of one-electron transfer mechanism caused the formation of some undesirable products, such as di-brominated phenoxyphenols and dihydroxylated biphenyls.

4.2 Dyes and dye wastewater

The application of Fe(VI) for removal of textile dyes is one of the promising technologies because it can act as an oxidant as well as a coagulant at the same time and it enhances the biodegradability property of dye. Li et al. [27] investigated the azo dye orange II removal by different types of Fe(VI), namely, potassium permanganate, potassium ferrate(VI) and the ferrate(VI) hypochlorite liquid mixture. It was observed that within 30 minutes, maximum discoloration of 95.6% was achieved with ferrate(VI) hypochlorite liquid mixture over a pH range of 3 to 11. Whereas, only 17.7% and 62 % of discoloration was observed respectively when only potassium permanganate and potassium ferrate(VI) were employed. However, one of the drawbacks of the above process is that residual hypochlorite in ferrate(VI) hypochlorite liquid mixture produces dangerous disinfection byproducts.

In another study, Xu et al. [28] utilized a highly stable composite ferrate(VI) solution produced by the chemical method with KOH at 65°C for the degradation of azo dye reactive brilliant red X-3B. The optimal conditions were found with dye concentration 0.08 mmol L⁻¹, pH = 8.4 and ferrate dosage 2.5 mg L⁻¹, giving discoloration of 99% after 20 min also; about 42% COD removal and 9% TOC removal were observed after 60 min. Also, the degradation pathway was theoretically established by the cleavage of by the C—N and N=N bond yielding muconic acid as the final reduced compound. In addition, the study by Turkay et al. [29] investigated the kinetics and mechanism of degradation of methylene blue by ferrate(VI). It was observed that about 96.82% methylene blue removal is achieved with initial methylene blue concentration of 50 mg L⁻¹, pH = 13.6 and ferrate dosage = 59.5 mg L⁻¹ over 35 minutes of reaction time and followed second-order kinetics.

4.3 Pesticides

Fe(VI)-based oxidation processes are effective in improving the biodegradability of wastewater containing persistent organic pollutants such as pesticides.

In a study conducted by Zhu et al. [21], the ferrate-based pretreatment of wastewater containing a higher concentration of alachlor improved its biodegradability and resulted in the total removal of alachlor within 10 min under optimized conditions. A comparison of the oxidation property of peroxymonosulfate (PMS) and Fe(VI) and for the degradation of atrazine was studied by Wu et al. [30]. They have observed a significant enhancement in the degradation of atrazine in Fe(VI)/PMS system when compared to Fe(VI) or PMS alone.

In another study conducted by Chen et al. [31], the combined oxidation ability of the UV/Fe(VI) system for the removal of an organophosphorus pesticide profenofos was studied. They have observed that degradation of the compound was dependent on the pH and Fe(VI) dosage, and the degradation progressed through de-ethylation and de-propylation with subsequent C—O cleavage with the release of orthophosphate. The effect of operational parameters such as pH, Fe(VI) dosage and other water constituents (anions and cations) was studied while evaluating the potential of Fe(VI) oxidant on parathion (PTH) degradation [32]. Under the operation condition of pH 7 and Fe(VI): PTH 15:1, 99% of removal was observed, the presence of Fe^{3+} , HCO_3^- , Cu^{2+} , HA, Ca^{2+} decreased the removal rate, while no significant effect was observed for Cl^- and NO_3^- . In a similar study conducted by Liu et al. [33], they have concluded that the degradation of chlorpyrifos was mainly through C=O cleavage and hydroxyl substitution reactions.

4.4 Pharmaceuticals

The presence of pharmaceutically active compounds in the aquatic environment can cause serious health issues to the living organism. The strong oxidation potential of Fe(VI) and its ability to remove nitrogen- and sulfur-containing compounds had gained attention for the removal of pharmaceuticals from wastewater. The kinetics of removal of an antibacterial drug sulfamethoxazole (SMX) using potassium ferrate oxidant was studied by Sharma et al. [34]. They found that the rate constants are pH-dependent, and at higher concentrations of potassium ferrate (10 μM), the half-life of the compound was found to be 2 min at pH 7. In a similar kind of study, when the kinetics of removal of antiphlogistic drug ibuprofen (IBP) was studied, the degradation rates decreased with an increase in pH, which was related to protonation of Fe(VI) [35].

Another study conducted by Ma et al. [36] used sodium-potassium ferrate for the removal of tetracycline hydrochloride (TC) antibiotics at different pH and molar concentrations. Although maximum degradation was observed within a pH range of 9–10 and at a molar ratio between 1:1 and 1:10 [Fe(VI):TC], only 15% mineralization of the compound was observed due to the formation of stable intermediate products. The toxicity and kinetics of diclofenac removal by Fe(VI) under simulated disinfection conditions were studied by Wang et al. [37], and they have observed a rapid increase of the inhibition rate of the luminescent bacteria due to the formation of toxic intermediates. Also, the toxicity of Fe(VI)-treated wastewater containing pharmaceuticals was assessed on zebrafish embryo by Jiang et al. [38] and found that the level of toxicity decreased after the treatment.

The combination of Fe(VI) treatment with radiation for the removal of carbamazepine was studied by Wang et al. [39] for increasing the degradation efficiency and mineralization. They observed an increase in TOC removal during simultaneous treatment. Although the overall degradation rate of carbamazepine decreased, enhanced mineralization was observed with the sequential treatment of radiation, followed by Fe(VI), which may be due to a decrease in pH of the solution from 7.0 to 5.4, where the Fe(VI) oxidation was higher. The performance of electrogenerated ferrate(VI) and solid form of Fe(VI) were compared for the

degradation of amoxicillin and ciprofloxacin [40]. By modeling the ferrate decomposition to understand its oxidation potential, they have concluded that the increased removal efficiency of compounds was due to the presence of a deprotonated form of ferrate ion.

In a study conducted by Yang et al. [41] for the removal of a mixture of emerging contaminants spiked in secondary effluent, only selective oxidation of electron-rich compounds was observed with Fe(VI)-based treatment process. Nevertheless, higher Fe(VI) exposure involved faster destruction of these recalcitrant compounds, proving the effectiveness of these treatments as an efficient tertiary treatment for broad-spectrum micropollutants in wastewater. In another study where mixture of four pharmaceuticals were treated with Fe(VI) (3 mg/L) all the compounds except bezafibrate were degraded effectively [42]. From this observation they have suggested that Fe(VI) is a selective oxidant, and the degradation efficiency will decrease if a carboxylic group is present in the compound.

4.5 Inorganic removal by ferrates

Fe(VI) became environmentally friendly oxidants due to its high oxidizing ability and did not produce any toxic compounds on decomposition. Therefore, the application of ferrates has been widely investigated among the researches for the removal of inorganics from water. Inorganic pollutants such as heavy metals, inorganic salts, trace elements and complexes of metals, among others, can also be removed by Fe(VI). There are basically two types of mechanisms in the ferrate oxidation of inorganic compounds, namely, one-electron transfer and two-electron transfer. Also, the degradation of inorganics is observed to be finished in milliseconds to seconds [19]. For instance, the study by Johnson and Hornstein [43] reported the complete oxidation of hydroxylamine to nitrous oxide by ferrates following a two-electron transfer oxidation mechanism, where the transfer occurs from either ferrates or water.

The application of ferrates for phosphate removal in municipal wastewater treatment plants is a feasible option and needed to be explored in detail. Lee and Zu [44] reported around 80% phosphate removal with a ferrate dose of 7.5 mg Fe L^{-1} . They investigated the performance of various forms of iron such as Fe(VI), Fe(II) and Fe(III) and observed that the efficiency of Fe(VI) is 1.5 times higher than Fe(III) because of the larger aggregate formation with Fe(VI) having higher specific surface. A similar study by Lee and Um [45, 46] utilized the combined use of Fe(III) and Fe(VI) for removal of arsenic by coagulation from river water samples and observed that 90% removal was achieved with an optimum dose of 2 mg L^{-1} Fe(VI) at pH 7.8. Also, potassium ferrate was used to remediate a solution containing a mixture of arsenic and antimony, where at first the compound was oxidized by Fe(VI) and then separated from the solution by the adsorption of its decomposition product [47]. In addition, the kinetics and mechanism of As(III) oxidation by Fe(VI) were studied by Lee et al. [45, 46], and they concluded that oxygen transfer mechanism in aqueous solution resulted in oxidation of As(III) to less toxic As(V).

Ferrate-based oxidation process was used for the removal of insoluble Cr(III) compounds from high-level radioactive tank waste, which was alkaline media [48]. $\text{Fe}_3\text{O}_4^{2-}$ concentration played a significant role in the Cr(III) removal; however, increasing the Fe(VI)/Cr(III) ratio greater than 10 reduced the removal efficiency. Ferrates are also capable of oxidizing organic metal complex species with its simultaneous removal from aqueous solutions [49, 50]. They are successfully used in industrial wastewater containing metal complexes, and treatment process efficiency

depends on pH and Fe(IV) dosage. Among the different metal complexes, zinc cyanide (CN) found in the effluent wastewater of metal finishing industries had a significant environmental impact.

The effect of Zn(II) on the removal of cyanide by Fe(VI) was studied by Yngard et al. [51] at different alkaline pH conditions. Although they have observed a decrease in the oxidation rate of cyanide in the presence of Zn(II), complete removal was achieved by Fe(VI). Another ferrate-based oxidation study was conducted by Lee and Tiwari [52] for the simultaneous removal of CN, CN-Cu and CN-Ni. They have observed that in the CN-Cu and CN-Ni systems, rapid oxidation of CN was observed, while a relatively slower degradation of CN was observed in the mixed CN-Cu-Ni. In another study, Ni(II)-CN and Ni(II)-CN-ethylenediamine-tetraacetate (EDTA) solutions were removed using Fe(VI) as a function of pH ranging from 8 to 11 [53]. The presence of an organic ligand EDTA enhanced the removal of cyanide in Ni(II)-CN-EDTA, while only 60% removal was observed with Ni(II)-CN metal-cyanide complex. The stronger complexes formed due to the addition of EDTA into the Ni(II)-CN metal-cyanide complex reduced the amount of additional Fe(VI) required to oxidize cyanide in it. A similar study conducted by Pachua et al. [54] assessed the suitability of ferrate(VI) for the simultaneous oxidation of Cu(II)-IDA and Zn(II)-IDA (iminodiacetic acid). It was observed that maximum removal Cu(II) or Zn (II) occurred at higher pH values.

4.6 Organic matter and wastewater

Fe(VI) can be effectively and efficiently used for removal of the organic matter present in wastewater. The stronger oxidizing property along with its disinfection and coagulation property makes Fe(VI) an ideal chemical for sewage treatment [55]. One of the main advantages of ferrate treatment is that it produces very less volume of sludge and thus makes sludge treatment much easier [56].

The study by Jiang et al. [12] investigated the applicability of ferrates for disinfection/coagulant and compared the performance with conventional disinfectants and coagulants such as sodium hypochlorite (NaOCl) and NaOCl combined with ferric sulphate or alum for the treatment of water and observed around 20% more removal with ferrates at a pH between 6 and 8. Among the three chemicals, ferric sulphate, potassium ferrate(VI) and aluminum sulphate used by Jiang et al. [55] for sewage treatment, maximum color removal and COD reduction were observed for potassium ferrate(VI). The dual properties of Fe(VI) species capable of oxidizing micropollutants and inorganics in wastewater were assessed for municipal wastewater treatment [57]. They have observed that Fe(VI) was efficient in oxidizing micropollutants and subsequently removing phosphate from a secondary treated effluent in a single treatment step.

In another study, natural organic matter (NOM) present in river and stream water was removed using potassium ferrate [58]. They have observed more than 70% removal of humic and fulvic acids by varying the Fe(VI) dosage, pH and temperature of the solution. The efficiency of ferrate and chlorine on removing organic matters present in secondary treated effluent was compared for two different wastewater treatment plants by Gombos et al. [59]. When comparing the bacterial inactivation, both Fe(VI) and chlorine were very effective even at their lower concentration, while a higher COD and TOC removal were observed for Fe (VI) in comparison to chlorine. The results showed that the higher oxidation capacity along with its coagulation and flocculation property of the reduced Fe(III) ions enhanced the wastewater treatment.

5. Ferrate as a disinfectant

Coagulation and disinfection are the two major unit operations that are important to ensure proper water quality. Disinfection has been known to be a tertiary treatment for the removal of pathogens. While coagulation destabilized the colloids and aggregates them, after which they can be settled and thereafter removed. Over the years, there has been rapid deterioration of the water quality due to increased water pollution. Hence, efficient chemical reagents and treatment techniques are required to meet stringent water quality standards. Various disinfection processes are used these days such as chlorination, UV irradiation and advanced oxidation processes [60].

The most common disinfection method used is chlorination. However, chlorine in the presence of organic substances such as humic acid is known to produce trihalomethanes (THM), which are known carcinogens. Ozonation results in the formation of N-nitrosodimethylamine (NDMA). While, presence of bromide ion also initiates formation of a potential carcinogen bromate [12, 13]. Thus, removing these disinfection byproducts is another challenge. An ideal chemical reagent would thus be a treatment reagent capable of carrying out both disinfections and should also be capable of oxidizing organic as well as inorganic pollutants such as heavy metals. Ferrate, with a redox potential of 2.2 V, higher than ozone (2.0 V), satisfies both requirements [61]. Ferrate is also considered as a “green” chemical. This is primarily because ferrate oxidation does not lead to the production of any harmful byproducts. The product of Fe(VI) oxidation is either ferric hydroxide or Fe(III) [14, 15].

5.1 Effect of ferrate ions on bacteria

Murmann and Robinson were the first to demonstrate the disinfection property of ferrate in the year 1974. The disinfection studies were conducted on two pure strains of non-recombining *Pseudomonas*, combining *Pseudomonas* and Missouri River Water. It was observed that complete killing of bacteria occurred at ferrate concentrations of 4, 50 and 100 ppm, respectively, for all the three tested samples. It was found that ferrate(VI) could kill 99.9% of microbes, such as *E. coli*, within 7 min of contact time and at a dose of 6 mg L⁻¹ at a pH of 8. Also, the disinfection ability enhanced when the pH was below 8. For the same concentration of bacteria, a contact time of 17 min was required in order to achieve the same level of disinfection when the ferrate concentration was reduced to 2.4 mg L⁻¹ [62].

The performance of ferrate as a disinfectant for drinking water was also compared with chlorine. Ferrate was found to achieve >6log₁₀ inactivation of *E. coli* at a very low dose of 6 mg L⁻¹, while 10 mg L⁻¹ of Cl₂ was required to achieve the same level of disinfection. Also, ferrate(VI) was found to work efficiently over a wide range of pH [12]. Similarly, for sewage treatment, potassium ferrate was found to achieve >4 log₁₀ inactivation of bacteria, while alum sulphate and ferric sulphate were able to inactivate only 1 log₁₀ and 1.5 log₁₀ bacteria. Also, the dosage of ferrate required was lesser than that of alum sulphate and ferric sulphate [55]. Effectiveness of ferrate as a disinfectant was also studied on aerobic spore-bearing bacteria, which suggested that sodium ferrate is a powerful disinfectant of this group of bacteria. The study showed that sodium ferrate was a better indicator than even chlorine [63].

Ferrate was also found to inhibit the dehydrogenase activity by inactivating the —SH radical and thus inhibiting both the exogenous and endogenous respiration of bacteria *Sphaerotilus*. The study suggests that intermediates generated during the ferrate decomposition penetrate the cell wall of the bacterium and inactivate the

—SH radical which is necessary for dehydrogenase activity and thus respiration of the bacterium. *Sphaerotilus* is known to cause bulking in activated sludge [64]. Clostridia resistant to chlorination were also found to be killed by ferrate. *Bacillus cereus*, *Streptococcus bovis*, *Staphylococcus aureus*, *Shigella flexneri*, *Streptococcus faecalis* and *Salmonella typhimurium* were also found to be susceptible to ferrate disinfection [4, 9, 10]. However, the gram-positive organisms are found to be more resistant to the ferrate action compared to gram-negative organisms such as *E. coli*.

5.2 Effect of ferrate ions on viruses

Effectiveness of ferrate as a disinfectant on virus removal was checked on human surrogate viruses such as MS2, f2, Q β and P22 bacteriophages [11–13]. Studies suggested that Fe(VI) was more efficient against naked icosahedral coliphages such as MS2 than gram-negative bacteria, *E. coli*. The k_i value for *E. coli* was reported to be 6.25×10^{-1} L/(mgFe \times min) (pH 7.2, 25°C), while the k_i value for MS2 inactivation was $2.27 (\pm 0.05)$ L/(mgFe \times min). The faster kinetics for virus inactivation might be because of the denaturation of the genome or transformation of the capsid proteins [65]. Furthermore, coliphages inactivation was found to be affected by pH and dissolved oxygen, thereby supporting the hypothesis stating that slower iron oxidation enhances virus inactivation. The adsorption of intermediates formed during the oxidation on the virus capsids was also necessary to inactivate the virus.

Heffron et al. suggested that coupling iron oxidation with regulated pH, similar to enhanced coagulation, will be able to achieve higher disinfection because of slow ferrous oxidation [66]. f2 and Q β were also found to be removed at a pH range of 6–8 by ferrate oxidation [9, 13]. Also, it was found that ferrate action is not as influenced by the disinfecting matrix compared to that of chlorine [67].

5.3 Effect of ferrate ions on algae

Eutrophication of lakes and rivers has increased rapidly due to discharge of the nutrients into the water bodies, specifically phosphate. Thus, removal of these algal blooms is now a major challenge in the drinking water treatment. Conventional coagulation is presently the method of choice for algal removal in the treatment processes. Copper sulphate and potassium permanganate are chemicals that are most commonly employed to control the algal blooms in lakes and rivers. Studies suggest that pretreatment with an oxidant enhances the algal removal on coagulation. Ferrate being an excellent oxidant was thus checked for algal removal. Algal removal on the addition of alum combined with ferrate pretreatment was found to improve the coagulation of algal cells [68].

It was observed that ferrate peroxidation enhanced the coagulation of algae by hampering the stability of algal colloids. Ferrate oxidation results in the formation of Fe(OH)₃. Fe(OH)₃ precipitates on algal cell surface resulting in increased weight and thus enhanced settleability. It was also hypothesized that on ferrate oxidation, the algal cells release certain exopolymer, which aids the coagulation. In a study conducted on *Microcystis aeruginosa*, it was observed that ferrate oxidation causes complete cell damage. Here the ferrate oxidation resulted in blocking photosynthesis by hampering the PSII functioning. The accumulation of excessive ROS further results in superoxidation of lipids, thereby increasing the cell permeability which finally results in complete cell damage of *Microcystis aeruginosa* cells. The removal of algae on ferrate was also influenced by pH and temperature. The removal efficiency was higher as the temperature increased, and also acidic pH enhanced the ferrate action on green algae [1, 10, 20].

5.4 Effect of ferrate ions on microcystins

Cyanobacteria such as *Microcystis*, *Anabaena*, *Aphanizomenon*, *Oscillatoria*, *Cylindrospermopsis* and *Lyngbya* are known to produce toxins, which affect aquatic life as well as human beings adversely. Some common toxins produced by cyanobacteria include anatoxin-a, anatoxin-as, aplysiatoxin, cylindrospermopsin, microcystin-LR, nodularin R and saxitoxin. Because of its adverse effects, US Environmental Protection Agency (EPA) in the year 2015 prescribed drinking water health advisories for microcystins and cylindrospermopsin. 0.3 mg L^{-1} was the prescribed limit for microcystins for preschool children, while the limit was 1.6 mg L^{-1} for school-age children.

The microcystins are composed of cyclic peptide ring of 7 amino acids and hepatotoxins, which are liver toxins. The peptide ring is composed of 5 non-protein amino acids and 2 protein amino acids. The microcystins' name is derived from these two protein amino acids. The most potent microcystin toxin is composed of leucine and arginine, thus the name microcystin-LR. Microcystin can remain in the water bodies from days to weeks, making it more dangerous. The toxicity of the microcystins is because of its Adda group [9, 14]. Ferrate essentially degrades the toxins by oxidation of the amino groups of microcystins. Thus, ferrate-induced degradation of algal toxins is greatly influenced by pH [69].

6. Conclusions

Ferrate [Fe(VI)] is a powerful oxidizing agent and can be used to remove organic and inorganic pollutants over a wide range of pH. Electrochemical synthesis of ferrate is the greenest and easiest method for high purity ferrate. The application of Fe(VI) for the removal of various recalcitrant pollutants such as pharmaceuticals, textile dyes, phenolic compounds, pesticides and inorganics, including heavy metals, is one of the promising technologies because it can act as oxidant as well as coagulant at the same time. The ability of ferrate to be an oxidant as well as coagulant also enhances removal of algae and microcystins. Also, ferrate is a potent disinfectant capable of removing bacteria as well as viruses. The action of ferrate, however, is dependent on pH and dissolved oxygen level of the media to be disinfected. The pH of the solution is one of the important factors which determines the stability and oxidation potential of Fe(VI). At higher pH values, the stability of Fe(VI) is higher as it increases the reaction rate with protonation of compounds. However, a high alkaline pH of liquid Fe(VI) causes the formation of harmful disinfection byproducts during disinfection treatment. Hence, a detailed research should be carried out for understanding the effect of pH in the treatment of various recalcitrant pollutants with different Fe(VI) concentrations.

Conflict of interest

The authors declare no conflict of interest.

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