

Application of Ferrate (VI) as Disinfectant in Drinking Water Treatment Processes: A Review

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Abstract: Due to the increase in the use of Ferrate (VI) or Fe(VI) as a multipurpose water treatment chemical, significant progress has been made in understanding the chemistry in aqueous solutions, with advances being made in such areas as the stability of Fe(VI) and the reaction kinetics and mechanism of Fe(VI) with various compounds in aqueous solution. It possesses a relatively high oxidizing capacity and the reduced Fe(VI) into iron(III) oxides/hydroxide again an important and useful precipitant, coagulant, flocculants and likely to be a good adsorbent via the formation of ferric hydroxide for various metal cations. Moreover, the non-toxic effect makes it to be considered as a green chemical and further enhances its widespread uses in various purposes. This paper attempts to review the applications of Fe(VI) as disinfectant in the treatment of drinking water and also its possible future applications in drinking water technology.

Key words: Ferrate • Disinfectant • Drinking Water • Coagulant • Disinfection By-Product

INTRODUCTION

Water has always played a prominent role in human civilization. When people first began settling in one place and growing crops for sustenance, it was invariably near water sources like lakes, rivers, or groundwater springs. Water is needed for drinking purpose, preparing food, bathing, cleaning, irrigating crops and a variety of other tasks, so it is important to have ready access to this resource. The water sources used for supplying water were not always clean however and treating drinking water to improve smell, taste, clarity, or to remove disease-causing pathogens has occurred in one form or another throughout record history. More than 1 billion people are without access to adequate sources of drinking water. Many people in the world suffer illness and death each year due to drinking water contamination [1, 2]. Recently, water not fully disinfected has caused outbreaks of

cryptosporidiosis in Milwaukee, Wisconsin (1993), *Escherichia coli* induced gastroenteritis in Walkerton, Ontario (2000) and cholera in Peru [3, 4].

Disinfection as a tertiary chemical treatment is widely adopted to remove harmful microorganisms in water and deliver safe drinking water to the community. Various kinds of disinfectants have been widely used for water treatment. These include chlorine, sodium hypochlorite, chlorine dioxide, chloramines, hydrogen peroxide, ozone, UV light, permanganate or their combination [5, 6]. However, there are some problems with the application of these disinfectants regarding the formation of potential harmful disinfection by-products (DBPs), e.g. trihalomethanes (THMs), bromates, haloacetic acid [7-10]. Chlorine dioxide destroys the aromatic and conjugated structures of dissolved organic matter (DOM) and transformed large aromatic and long aliphatic chain organics to small hydrophilic [11]. Oxidation of DOM with

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chlorine dioxide also generates organic by-products such as aldehydes and long chain carboxylic acids [12]. The DBPs that have been observed in chlorinate water include haloacetonitriles, halonitromethanes, halo ketones and chloral hydrate [11, 13 & 14]. Nitrosamines such as N-nitrosodimethylamine (NDMA), a suspected human carcinogen are formed when monochloramine is used for disinfection [15]. This research has caused alarm in the treatment industry because the main purpose of monochloramine application as disinfectant is to avoid toxic by-products. Chlorine dioxide (ClO_2), however, does not produce significant amounts of halogenated organic DBPs [16]. Chlorite (ClO_2^-) and chlorate (ClO_3^-) are the major products; approximately 70% of applied ClO_2 forms chlorite, while about 10% forms chlorate [17]. Due to the health concerns over chlorite and chlorate, the maximum contaminant level (MCL) for chlorite in drinking water is regulated at 1 mg/L in the United State [18]. Recently, Chinese sanitary standard for drinking water had been reviewed. Concerning chlorite and chlorate, the threshold is 0.7 mg/l [11]. UV disinfection and/or treatment with combined chlorine are increasingly being applied as alternatives to control chlorine resistant microorganisms and regulated DBPs, respectively [19]. This industry trend has increased concerns about viral pathogens, especially enteric viruses, because of their greater resistance to UV light and combined chlorine than to free chlorine [20, 21]. Furthermore, recent reports indicate that combined chlorine disinfection processes promote increased formation of unregulated, but potentially more toxic, DBPs [22, 23].

Treatment success using these disinfectants depends on the source water conditions such as pH and the existing levels of bromine, iodide and natural organic matter (NOM) [2]. For example, ozone can reduce levels of THMs and haloacetic acids (HAAs), but it can form the potent carcinogenic bromate ion by reacting with bromide present in water [24, 25]. In order to meet the more stringent regulations/standards of drinking water, an ideal treatment chemical reagent should be developed and assessed, which should not form any harmful by-products in the treatment processes but give more efficient inactivation of microorganisms, partially degrade and oxidize the organic and inorganic impurities and remove colloidal/suspended particulate materials and heavy metals.

Ferrate (VI) [FeO_4^{2-}], is environmentally friendly treatment ion that can meet these new challenges confronting the drinking water industry. Recently, attempts have been made to review ferrate (VI) as

disinfectant in water treatment technology. However, these attempts were much generalized in the wastewater industry. Sharma *et al.* [2] reviewed excellent properties of ferrate (VI) to kill a wide variety of bacteria and virus in water and wastewater treatment processes. The use of potassium ferrate was discussed for the treatment of wastewaters particularly its disinfection property and reported that it can reduce 50% more color ($\text{ViS}_{400\text{-abs}}$), 30% more COD and kill 10% more bacteria in wastewater as compared to aluminum sulfate and ferric sulfate [26]. In our knowledge, it is the first time the review of ferrate (VI) as disinfectant focused only in drinking water is available. In this paper, the potential role of ferrate (VI) as disinfectant in drinking water treatment processes and the current state of the art associated unique chemistry of these high-valence states of iron were reviewed.

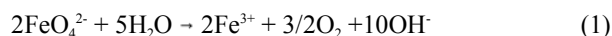
Properties of Ferrate (VI) Oxidant: Iron commonly exists in two oxidation states, +2 and +3, however, in a strong oxidizing environment, higher oxidation states of iron, +6 can be obtained [27]. The chemistry of iron with high oxidation states [Fe (VI)] in aqueous solution has been of interest because of his implication in numerous hydroxylation/oxidation reactions of environmental, industrial and biological importance [28]. Recently, a number of papers have been published on the detailed reaction mechanisms of Fe (VI) ion (especially, FeO_4^{2-} oxidations). Most of them paid their attention to the novel properties of the chemical such as high oxidizing power, reaction selectivity, stability as a salt and production of non-toxic by-products (e.g., Fe (II) and Fe (III)). Fe (VI) ion is a powerful oxidizing agent throughout the entire pH range with a reduction potential varying from +2.2 to +0.7 V in acidic and basic solutions, respectively [29]. With its high oxidizing power which is greater than any other disinfectants (Table 1) and it is potentially the strongest of all the oxidants/disinfectants realistically applicable to water treatment; Fe(VI) can oxidize various organic and inorganic compounds. For example; Fe (VI) is applied to oxidize biphenol A and steroid estrogens [30]. N-nitrosodimethylamine (NDMA) precursors are oxidized by ferrate (VI) [31]; the oxidation of carbamazepine, an anticonvulsant drug is widely detected in surface waters and sewage treatment effluents, by potassium Fe (VI). The results show that Fe (VI) rapidly oxidize carbamazepine by electrophilic attack at an olefinic group in the central heterocyclic ring, leading to ring-opening and a series of organic oxidation products [32], oxidation of glycine and glycylglycine by using ferrate (VI) and the reactivity of Fe (VI) with Gly and Gly-gly indicates the significant

Table 1: Oxidation potential of different disinfectants [38]

Disinfectant	Reaction	E° (V)
Chlorine	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.358
	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	0.841
Hypochlorite	$\text{HClO} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$	1.482
Chlorine dioxide	$\text{ClO}_2(\text{aq}) + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954
Perchlorate	$\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$	1.389
Ozone	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.076
Hydrogen peroxide	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.776
Dissolved oxygen	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.229
Permanganate	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.679
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.507
Fe(VI)	$\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$	2.20

E° (V): Oxidation potential

potential of Fe (VI) to remove amine- and peptide-containing pollutants in water and wastewater [33]. Karlesa *et al.* [34] studied Fe (VI) oxidation of β -Lactam antibiotics and they found that Fe (VI) oxidation appears to be effective as a means of lowering the antibacterial activities of β -Lactams. Sharma [35] studied the oxidation of inorganic compounds by Fe (VI). As for the stability, Fe (VI) remains stable for hours within the pH range 9-10, but slowly reacts with water to generate ferric ion and oxygen [36, 37] Eq.(1):



Below pH 9, however, Fe (VI) is unstable and decays rapidly into ferric ion (auto-decomposition) within seconds to minutes, following a second-order kinetics with respect to Fe (VI) itself [39]. The rate of auto-decomposition of Fe (VI) increases with decreasing pH, which has been ascribed to the protonation of FeO_4^{2-} that are more reactive [39]. The potential advantage of using Fe (VI) in water treatment processes is the fact that it does not produce any toxicologically harmful by-products unlike conventional disinfectants such as chlorine [40]. Therefore, Fe (VI) is often cited as an effective alternative oxidant/disinfectant for water and wastewater.

Coagulant: Ferrate (VI) is also added as a coagulant for water and wastewater treatment processes [38]. Fe (VI) has proven itself to be an efficient coagulant for removing various toxic metals, non-metals and radionuclides [37, 41]. Coagulation destabilizes colloidal particles and transfers small particles into large aggregates and adsorbs dissolved organic materials onto the aggregates, which can then be removed by sedimentation and filtration [42]. In addition, several studies have shown that Fe (VI) could play the multiple roles of oxidant, coagulant and disinfectant simultaneously for the treatment of drinking

waters and wastewaters [37, 43- 46] (Table 2). For example, Fe (VI) was successfully used in a novel arsenic removal process because of its dual functions of an oxidant and a coagulant [46]. Due to the increasing interest in the use of Fe (VI) as a multipurpose water treatment chemical, significant progress has been made in understanding the chemistry in aqueous solutions, with advances being made in such areas as the stability of Fe (VI) and the reaction kinetics and mechanism of Fe (VI) with various compounds in aqueous solution [11, 37, 47 & 48]. Conventional/common coagulants used for water treatment include ferric sulfate, aluminum sulfate and ferric chloride (Table 3). However, these common used chemical reagents have shown their limitation [49]. In many ways, the addition of Fe (VI) is much like the combined use of pre-ozonation and alum coagulation, the later having been much more intensively studied. Low doses of a strong pre-oxidant can result in direct oxidation and possibly better removal by subsequent coagulation via a number of postulated mechanisms [50]. By analogy, one would expect high doses of Fe (VI) to excessively oxidize the NOM rendering it less adsorbable to ferric floc, much as ozone does [50]. The analogy between ozone and Fe (VI) is not perfect, however. Differences include the unavoidable coupling of oxidant dose with coagulant dose when both are a result of the same chemical addition (i.e., Ferrate). Also, higher reactivity of Fe (VI) at low pH is in contrast to ozone, which undergoes more rapid decomposition forming hydroxyl radicals at high pH. Also, it's quite likely that the initial ferric hydroxide precipitate is different between the ferrate and ferric system. In the former case, Fe (III) is generating in-situ at lower rates as pH increases. This is probably not the case with ozonation-coagulation as the coagulant is added in the same fashion regardless of whether it is preceded by ozone [50].

Disinfectant: Disinfection is designed to kill harmful organisms (e.g., bacteria and protozoan) and oxidation is used to degrade various contaminants. Fe (VI) has been found to effectively inactivate bacteria (*Escherichia coli*, *Sphaerotilus*, *Bacillus subtilis*, *Bacillus licheniformis* RB1-1B, *Mycobacterium frederiksbergense* M8-6, *Mycobacterium setense* M9-4) [29, 52 & 54], viruses (ϕ 2 coliphage, Q β -coliphage and Bacteriophage MS2) [55-57], algae (Microcystin-LR) [58] and other pathogens [59] in synthetic buffer solutions and secondary effluents. These studies have revealed that Fe (VI) could inactivate = 99.9% of different microorganisms (that corresponds to 3 orders of magnitude reduction of initial concentration)

Table 2: Water treatment technology [50]

	Chlorine	Hydrogen Peroxide	Ozone	Ferrate
Oxygen atoms	None	2	3	4
Redox potential	1.39	1.78	2.08	2.20
Coagulant	No	No	No	Yes

Table 3: Comparative performance of coagulants at optimum dose [51]

	Aluminum sulfate	Ferric sulfate	Ferrate(VI)	
pH	6.75-7.48	6.75-7.48	5	7
Optimum dose as ion(mg/L)	8	22	15	22
Optimum dose as ion (mM/L)	0.30	0.39	0.22	0.39
Suspended solids removal (%)	91	95	89	94
Color (ViS ₄₀₀ -abs) removal (%)	50	50	100	92
Total COD removal (%)	7	18	43	32
Bacteria inactivation (%)	90	91	>99.99	>99.99

Table 4: Disinfection of water by potassium ferrate (VI) that achieved more than 99.9% reduction of total coliform bacteria [2]

Source	pH	Suspended solids (mg/L)	NH ₃ -N (mg/L)	COD (mg/L)	Total coliform (MPN ml) (prior to disinfection)	Doses as Fe in K ₂ FeO ₄ (mg/L)	Reference
Lake water, UK	3.5-7.5	-	-	-	1.2-2.1 × 10 ²	0.5	[61]
Lake water, Turkey	6.5	15.6	0.295	43.4	50 × 10 ⁴	2.5	[62]
River water1	7.3	19.8	6.40	14.5	4.1 × 10 ⁴	3.1	
River water2	7.4	6.20	8.70	5.00	1.1 × 10 ³	2.3	
River water3, Japan	7.3	2.40	0.20	1.20	2.1 × 10 ²	0.6	

both in laboratory-scale and in pilot-scale experiments with relatively low applied reagent dose [54]. Moreover, many researchers have tested the removal of total and fecal coliforms by Fe (VI) [60, 61]. Fe (VI) treatment of water sources collected worldwide can also achieve more than 99.9% kill rate of total coliforms (Table 4). Source water characteristics such pH, suspended solids, chemical oxygen demand (COD) and NH₃-N of the tested samples were all different [2]. The results in Table 4 indicate that the amounts of Fe (VI) required for complete destruction of coliforms varied with the initial number of microorganisms in water before treatment with Fe (VI) [2]. Gilbert *et al.* [49] studied the comparative disinfection performance at pH 8 of Fe (VI) and sodium hypochlorite with ferric sulfate for 30 min contact time and for various doses. They have observed that 4 mg/L ferric sulfate with 10 mg/L Cl₂, or, 8 mg/L ferric sulfate with 8 mg/L Cl₂, were required to achieve 100% inactivation of *Escherichia coli*, whilst a small Fe (VI) dose of 6 mg/L as Fe was needed to achieve the same target. The results demonstrated that in

order to achieve 100% inactivation, the relatively lower doses of Fe (VI) was required in comparison with ferric sulfate plus Cl₂. Even though they have similar redox potentials, Fe (VI) was found to be substantially less effective at inactivating *Bacillus subtilis* spores as compared to ozone [29]. These authors attribute the difference to the decomposition precipitation of Fe (III) on the spores coat layer, which could protect the spore from further oxidation.

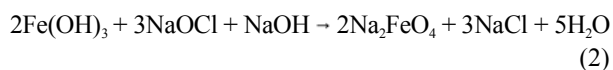
Existing Knowledge in the use of Ferrate (VI) in Drinking Water Treatment Processes: In this modern century, many people continued to suffering or dying because of the lack of safe drinking water worldwide. Even developed countries such as United States (US) and Canada for example, still having drinking water problems [17]. On this regards, researchers around the world paid more attention to this by developing new technologies that will replace the conventional technologies.

Fe (VI) is a powerful oxidant and disinfectant that has been proposed for use in drinking water treatment in the U.S. for more than a decade [63]. In many ways, it can be considered affordable, simple alternative to ozonation and thus it is well suited for use in small systems. Like ozone and other disinfectants such as chlorine dioxide and chloramines, Fe (VI) is highly selective oxidant, but it does not lead to the formation of any known hazardous by-products (brominated or chlorinated DBPs, bromate or chlorite). Despite its effectiveness and cost-effectiveness, Fe (VI) has only recently been used at full-scale for the first time in the U.S. (Florida groundwater plant) [63]. Until recently, a major impediment to its use has been the lack of availability of Fe (VI) [5]. This obstacle seems to be rapidly disappearing, as several business ventures have been launched to fill the gap. One such company is already offering full-scale units for on-site production (Ferrator®) and their officials cite a cost of only \$ 0.06, or about 2% of the average water charge in Massachusetts (Ferrate Treatment Technology, LLC). Ferratec (Battelle's) licensed the process and now with partner Electrosynthesis, has successfully completed pilot-scale trials and is ready to move to full-scale production. There are competing technologies under development (e.g., electrochemical methods) and a flurry of US patent applications. Now it appears that the biggest impediment is the lack of independent, unbiased information concerning Fe (VI) full impact on treatment systems and finished water quality [5].

Ferrate is considered to be a 'green' chemical for use in water treatment [64]. This is partly because it does not produce any known toxic by-products. The end product of Fe (VI) oxidation is relatively benign ferric sludge and oxidized forms of water contaminants. Among the latter are oxygenated NOM molecules and compounds that are more readily biodegradable. Moreover, Fe (VI) may be produced using standard chemicals that are often present in water treatment plants (ferric coagulants, caustic and in some technologies, chlorine) and its use is thought to reduce the subsequent needs for these chemicals.

Fe (VI) is relatively unstable in the presence of moisture and therefore it is considered most practical to generate it on site near the point of use. Three general methods are available to synthesize Fe (VI), all from readily-available starting materials of good stability and all using alkaline conditions [63]. These include: (1) the electrochemical method, (2) the high-temperature dry oxidation method and (3) the ambient temperature wet oxidation method.

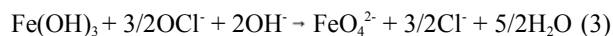
The electrochemical method involves the oxidation of iron anode in an electrochemical cell. Old researchers described this method using diaphragm cells. Recently, patents have been filed for the production of Fe (VI) by membrane cells [65]. Several dry processes are described in the literature [66]. The oldest method is the combustion of iron scraps with potassium nitrate at high temperature [67]. Several other methods involve the mixing of alkali peroxide (Na_2O_2 or K_2O_2) with iron salt, most often an iron oxide, at high temperature. These methods were developed in laboratory using expensive chemicals and are difficult to scale-up. In the wet method, the oxidation of iron salt (iron hydroxide or iron sulfate) is carried out in strong alkaline solution with a chlorine gas or strong soluble oxidizer (hypochlorite of sodium or potassium) [68, 69].



The addition of excess solid potassium hydroxide can precipitate out of solid potassium Fe (VI). These methods do not produce solid potassium Fe (VI). The Fe (VI) solutions are not very stable and decomposition is very sensitive to temperature and to the presence of impurities. The solid potassium Fe (VI) is not very pure and presence of impurities such as KCl and KClO_3 has been detected [70].

The first and third methods are the ones considered most practical for drinking water applications. Electrochemical methods have been the subject of many recent publications in the open literature [71-75]. In contrast there has been less openly-published material on the wet oxidation method, even though this is the method of choice among water treatment researchers doing bench-scale studies. Modern laboratory methods using room-temperature wet oxidation achieve 50-70% yields with a final crystalline product of 99% purity [76]. Stability and probably yield can be improved with exclusion of trace metals that can catalyze Fe (VI) decomposition. There is little doubt that proprietary studies have been conducted by firms wishing to commercialize this technology such as Ferrate Treatment Technology (FTT). The FTT technology uses ferric chloride, caustic and sodium hypochlorite to produce aqueous Fe (VI) in an on-site reactor. According to the FTT, wet oxidation method can produce Fe (VI) at less than 10% of the cost of acquiring commercial dry Fe (VI). FTT has positioned its liquid Ferrate technology to be exploited as revolutionary new green treatment chemistry

because it is environmentally friendly and powerful enough to meet escalating treatment demands, cost-effective to operate and maintain, can be synthesized from commodity feedstock's, utilizes existing plant infrastructure and plugs into existing treatment processes, highly scalable, modular and easy to retrofit and implement, requires a small footprint; critical for landlocked treatment facilities and requires minimal incremental capital investment compared to UV or ozone.



Many studies conducted by researchers showed the effectiveness of Fe(VI) for oxidation of metals, non-metals and organic contaminants in water treatment. These include ammonia, cyanide, thiocyanate and sulfide [47], iodide [35], arsenic [46], phenol [77, 78], estrogens [31, 79], bisphenol A [31, 80], pharmaceuticals [31, 81& 82], microcystin [83], Triclosan [84] and benzotriazoles [85]. Sharma *et al.* [81] Conducted comparative studies of 5 oxidants commonly used in drinking water treatment. They concluded that Fe (VI) was more efficient to transform phenol-containing than olefin- and amine-containing compounds. Nevertheless, most organic amines will degrade in the presence of relevant levels of Fe (VI) [35].

Addition of Fe (VI) also results in elevated levels of biodegradable organic compounds. Bartzatt and Carr [86] found nearly identical formation of assimilable organic carbon (AOC) when equimolar doses of ozone and Fe (VI) were applied to Lake Zurich water (Switzerland). These authors also measured oxalate formation and found a linear relationship with dose that differed between Fe (VI) and ozone (1% molar yield vs 4%). For reasons that are not well understood, ozone produced AOC that is richer in oxalate than does Fe (VI). This means that much like ozone, Fe (VI) treatment should be followed by biological treatment, generally biologically-active filtration. This is very much in accord with the need to remove residual ferric solids by filtration.

CONCLUSIONS

Ferrate (VI) is found to be potentially applicable in drinking water treatment technology due to its strong disinfection capability. A number of publications demonstrated that Fe (VI) is a very strong, environmentally friendly oxidant and disinfectant in a wide pH range. The oxidation-reduction potential of Fe (VI) under acidic conditions is the highest among the

often used water treating oxidants (such as chlorine, hypochlorite, chlorine dioxide, ozone, hydrogen peroxide). The product formed during Fe (VI) reduction is Fe (III), which is not harmful or toxic for humans and the environment. Moreover, it does not remain in the treated samples, since Fe (III) is separated as ferric-hydroxide precipitate from the water-phase and serves also as a potential adsorbent or as a coagulant/flocculant in the subsequent treatment process. Ferrate (VI) is an emerging multifunctional agent for disinfection, oxidation and coagulation that can make a meaningful contribution to addressing the challenging demands of sustaining the water supply in the 21st century.

The high pH of treatment water with alkaline ferrate solution remains a great concern. There are still challenges in terms of ferrate synthesis, stability control, mechanisms of action and large scale applications. Solid Fe (VI) requires special storage and packaging to avoid exposure to humidity, which decomposes it to Fe (III). A complex approach that stabilizes Fe (VI) for few weeks in aqueous medium may enhance opportunities to utilize Fe (VI) in treatment processes. However, the large scale production of Fe (VI) would require additional research to resolve engineering and economic challenges.

Adequate progress has been made in understanding the mechanism of the reactions of Fe (VI) in alkaline medium. However, similar studies are almost unknown under acidic conditions and limited studies conducted so far have shown no clear trends. Therefore, delineation of the mechanism of the oxidative chemistry of Fe (VI) in acidic solution can be made by extending the kinetic and product studies; the involvement of different protonated species of Fe (VI) and pollutants in the oxidative mechanism will be clarified.

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