

# Ferrate(VI) in the Treatment of Wastewaters: A New Generation Green Chemical

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## 1. Introduction

Fresh water resources are under tremendous stress throughout the globe. Many areas all along the developing or even developed nations indicated, the fresh waters are greatly contaminated by the discharge of untreated sewage/industrial effluents and even variety of toxins entering naturally. Environmental regulations and public health concerns stated that wastewaters collected from municipalities and communities supposed to be treated as to meet the standards given prior its discharge/disposal into the aquatic environment. An advanced primary treatments aiming to enhanced the removal of colloidal particles and organic constituents from wastewaters, known to be an essential primary step and a starting point leading to fewer remaining particles and organic/inorganic contaminants, which in turn favorable for subsequent biological or physico-chemical treatment process. It is observed that the coagulation and oxidation/disinfection are two important unit processes for water treatments. Coagulation destabilizes colloidal impurities and transferred small particles into large aggregates and facilitates the several dissolved contaminants to adsorb onto the surface of these aggregates, which can then be removed by sedimentation and filtration. Disinfection is design to introduce the chemical dose enabled to kill the harmful organisms' *viz.*, bacteria, pathogens and viruses etc. from the wastewaters. Additionally, the usual method of sewage/municipal or even several industrial waste effluents treatment processes contained with large amount of sludge having various organic and inorganic compounds occurred, pose serious safety and quality aspects related to environmental concerns. Further, the final dewatered sludge (often called biosolids), which is to be land applied, endocrine disruptors and odors of the solids as well as pathogens have been brought under the serious attention towards its impact of the biosphere. However, such biosolids once treated carefully, may serve as an economic values as a soil conditioners and fertilizers etc. Further, the usual sludge handling processes *viz.*, thickening, drying, digestion and lime stabilization contribute to the on-site odors, became a severe environmental burden. Different types of organic sulfides and amines are produced in wastewater treatment facilities to give unpleasant odors. These processes are not effective in destroying toxic components of sludge *viz.*, endocrine disruptors and potential pathogens.

Complaints of illness related to the land application of biosolids are found to be increased at several places.

Similarly, the increased level of pharmaceuticals caused for enhanced level of its occurrence into the aquatic environment. Studies implied that the pharmaceuticals in surface waters and their existence in the environment may result in ecotoxicological effects. Ozonation and filtration with granular activated carbon or even advanced oxidation process (AOP) are commonly known technological implications for its removal or oxidation. In a line the heavy burden of surfactants are not directly toxic, but they inhibit both settling of floating particles and dissolution of atmospheric oxygen into natural waters. The biodegradation of several surfactants are seemingly slow in the wastewaters treatment plants.

The wastewaters treatment processes included in general the screening/skimming, followed by the biological/chemical treatment. Further, the advanced treatment methods composed with disinfections. Hence, the treatment process possessed with several steps comprising of variety of potentially needed chemicals. It is noteworthy to mention that sometimes the chemicals used, caused for release/discharge of harmful/toxic chemicals, and ultimately made additional burden to the environment. The applications of these chemicals restricted or even banned for its use in the environmental remediation particularly in the treatment of waste waters. Therefore, the use of conventional treatment methods required to be modified with adequate selectivity/suitability possessed with optimum efficiency but composed with more environments friendly. In a line the role of ferrate(VI) seems to be one of possible alternatives to be used for such treatment methods. The interesting chemistry of ferrates intended it to various possible applications in diverse area of research. However, its application in wastewaters treatment is known to be promising way of treatment showed several interesting observations. Recently, Sharma [1] has reviewed the extrinsic properties of ferrate in solution along with mechanistic and kinetic evaluation of the use of ferrate towards several inorganic pollutants.

### 1.1 Ferrate(VI)

Iron is one of very common element present in nature mainly as elemental iron Fe(0) along with the ferrous (Fe(II)) and ferric (Fe(III)) ions. The minerals of ferrous and ferric oxides further include the wuestite, hematite, magnetite, goethite, akagameite etc. (Table 1). Further, the iron and iron oxide based materials showed immense applications in different area. Some of the possible applications are magnetic pigments in recording, catalysis and magnetic fluids etc. Amorphous iron oxides potentially applied in industrial and water purification technologies. The photocatalytic processes includes the amorphous iron-oxide as an electrode, transforms water into hydrogen peroxide which further available for effective degradation of degradable impurities. Recent years, iron/iron oxides in the form of nano-particles showed unique properties for many advanced technological applications. Nano-particles of iron and iron-oxides in combination of oxygen and hydrogen peroxides are capable of oxidizing recalcitrant compounds. Salts of hypoferrite and ferrite as reported in Table 1 synthesized because of their use as magnetic materials in the modern electronic industry *viz.*, microwave devices, memory cores of compounds, radar and satellite communications and usage as permanent magnets.

In addition to three stable oxidation states of iron i.e., 0, +2 and +3, the strong oxidizing environment caused for the occurrence of higher oxidation states of iron *viz.*, +4, +5, +6, +8 etc. These higher oxidation states of iron are commonly known as ferrates. Among these

ferrates the +6 state is relatively stable and easy to synthesize hence, during last couple of decades greater interest and several research studies conducted using the +6 state of iron. Additionally, some *in situ* studies conducted with +4 and +5 oxidation state of iron. The reactivity of +5 and +4 oxidation state of iron is relatively high comparing to the +6 state. Ferrate(VI) which was first observed by Stahl in 1902 when he conducted an experiment detonating a mixture of saltpeter and iron filings, and dissolved the molten residue in water. This colored solution was subsequently identified as potassium ferrate(VI) ( $K_2FeO_4$ ). Eckenber and Becquerel in 1834 detected the same color when they heated red mixtures of potash (potassium hydroxide) and iron ores. Similarly, in 1840, Fremy hypothesized this colour to be an iron species with high valence, but its formula was suggested  $FeO_3$  [2]. Moreover, because of its stability and cumbersome of its synthesis, it was not used and studied further. However, some 100 years before systematic studies on ferrates started and explored the various applications of these compounds.

Compound	Name	Mineral/Salt
FeO	Ferrous oxide	Wuestite
Fe <sub>2</sub> O <sub>3</sub>	Ferric Oxide	Hematite
Fe <sub>3</sub> O <sub>4</sub>	Ferrosferric oxide	Magnetite
Fe <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O	Ferric oxide monohydrate	Goethite
FeOOH	Ferric oxyhydroxide	Akaganeite
FeO <sub>2</sub> <sup>2-</sup>	Hypoferrite	Na <sub>2</sub> FeO <sub>2</sub>
FeO <sup>2-</sup>	Ferrite	NaFeO <sub>2</sub> , KFeO <sub>2</sub>
FeO <sub>3</sub> <sup>2-</sup>	Ferrate(IV)	Na <sub>2</sub> FeO <sub>3</sub>
FeO <sub>4</sub> <sup>4-</sup>	Ferrate(IV)	Na <sub>4</sub> FeO <sub>4</sub>
FeO <sub>4</sub> <sup>3-</sup>	Ferrate(V)	K <sub>3</sub> FeO <sub>4</sub>
FeO <sub>4</sub> <sup>2-</sup>	Ferrate(VI)	Na <sub>2</sub> FeO <sub>4</sub> , K <sub>2</sub> FeO <sub>4</sub>
FeO <sub>5</sub> <sup>2-</sup>	Ferrate(VIII)	Na <sub>2</sub> FeO <sub>5</sub>

Table 1. Iron oxide compounds at different oxidation states of iron

## 1.2 Preparation of Ferrate(VI)

Three different preparation methods are known for Fe(VI) preparation in laboratory. These are:

- i. Dry oxidation of iron at high temperature
- ii. An electro-chemical method
- iii. Wet oxidation of iron(III) using chemical oxidizing agents

Briefly these methods are described here:

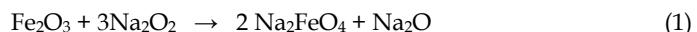
### i. Dry oxidation of iron at high temperature

Initially the ferrate(VI) was obtained by heating the iron filings with nitrates or the mixture of iron oxides with alkali and nitrates at temperatures of red heat. The final mixtures includes the ferrate(VI) salts, by-products and remaining reactants. Later, very systematically several metal salts of Fe(VI) obtained which are described briefly:

Sodium ferrate(VI) was obtained by taking  $Fe_2O_3$ -NaOH-Na<sub>2</sub>O<sub>2</sub>-O<sub>2</sub> at different temperatures. Moreover, the fusion of Na<sub>2</sub>O<sub>2</sub> with Fe<sub>2</sub>O<sub>3</sub> at a molar ratio under dry oxygen conditions at high temperature, yields sodium ferrate(VI). Ferrate(VI) yield which depends on the initial reagent molar ratio and temperature conditions. The entire process to be

conducted in a dry glove box and in presence of diphosphorouspentaoxide ( $P_2O_5$ ) and using high purity iron oxide (99.9 mol %). This was heated prior to use in dry oxygen at 150-200 °C as to remove sorbed water. This dried iron oxide was mixed with alkali metal peroxides and placed in a silver crucible for further thermal treatment. The 100% yield of the ferrate(VI) as in the form of  $Na_4FeO_5$  was obtained at the molar ratio of  $Na:Fe = 4:1$  at the exposition temperature of 370 °C for more than 12 hours.

Similarly, Fe(VI) was prepared using the galvanizing wastes as the wastes were mixed with ferric oxide in a muffle furnace at 800 °C for a while and the sample was cooled and stirred with solid sodiumperoxide and heated gradually for few minutes. The mixtures were melted and then cooled resulting with the formation of sodium ferrate(VI):

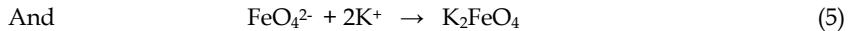
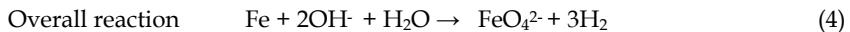
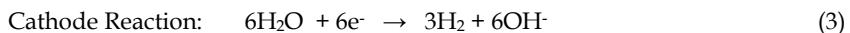


On the other hand potassium and cesium ferrate(VI) was prepared reacting with the superoxides of potassium and cesium with iron oxide powder at elevated temperatures of about 200 °C and the exposition time of  $Ca 10$  hours.

It can also be prepared at room temperature by mixing iron(II) or iron(III) salt with an oxidizing chlorine-containing agent in a strong base such as potash or soda. The ferrate(VI) thus obtained show the formula  $M(Fe,X)O_4$ , where M denotes to two atoms of Na or K or one atom of Ca or Ba, and X corresponds to atoms whose cation has the electronic structures of a rare gas.

### *ii. An electro-chemical method*

Ferrate was first prepared electrochemically in 1841 by anodic oxidation of iron electrode in strongly alkaline solution [3]. The basic principle of ferrate production by electrochemical method is the dissolution of iron anode in the electrolysis process having a strongly alkaline electrolyte solution. Hence, the preparation of ferrate consists of a sacrificial iron anode in an electrolysis cell containing a strongly alkaline solution of NaOH or KOH having electric current serving to oxidize the dissolved iron to Fe(VI) (Fig. 1). The possible anodic and cathodic reactions involved are;



Different mechanism are proposed for the formation of ferrate(VI). Christian [5] assumed that the reduction proceeds stepwise first to Fe(III), then to Fe(II) and finally to Fe(0). However, the three steps mechanism based on intermediate formation are proposed as [6]:

- a) The formation of intermediate species
- b) The formation of ferrate and the passivation of the electrode
- c) The formation of passivating layer that prevents further ferrate generation

The electrochemical production of Ferrate(VI) gives high purity of the product and the anodic polarization of iron electrode in the molten hydroxides is more adequate as compared to the classical electrolysis in water since water decomposes ferrate(VI) and passivation greatly reduced in this environment. The current yield during electrochemical

production increased with the carbon content in the iron anode material used; current yields were 15% for raw iron, 27% for steel and 50% for cast iron at a current density of  $10 \text{ Am}^{-2}$  with the NaOH concentration of 16.5 mol/L. Moreover, a current efficiency greater than 70% was achieved in preparing the ferrate when silver steel with carbon content of 0.09% was used. However, with the same conditions, the current efficiency was reduced to 12% when an alloy with a carbon content of 0.08% was used [7,8].

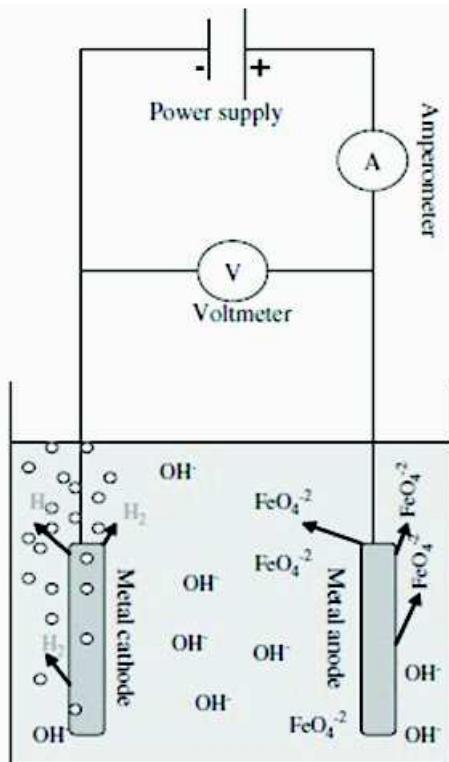


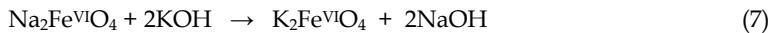
Fig. 1. Electrochemical cell used for Ferrate synthesis [4].

Bouzek optimized the optimum conditions for ferrate production particularly the anodic iron behavior in respect to the anode composition and the influence of the anode material used in highly concentrated NaOH solutions [9]. Previously, the sinusoidal alternating current was used to synthesize the ferrate electrochemically [10-12]. The electrodes used were 99.95 % pure of iron with 14 mol/L NaOH solution as electrolytes and the temperature was kept between 30 and 60 °C. These results revealed that the maximum current efficiency for generating the ferrate was 43% at the conditions adopted (a.c. amplitude 88 mA/cm<sup>2</sup>, a.c. frequency 50 Hz and temperature 40 °C).

### *iii. Wet oxidation of iron(III) using chemical oxidizing agents*

Wet chemical method includes the oxidation of ferric ion by sodium hypochlorite solution (preferably with higher concentration i.e., more than 12%) in presence of sodium hydroxide which may yield the sodium ferrate(VI) followed by the recrystallization with potassium

hydroxide yields potassium ferrate(VI). Reactions involved in the preparation process are given as:



This procedure produces 10-15% yield of potassium ferrate(VI) and many separation steps with several recrystallization steps including washing with dry methanol are required to obtain more than 90% purity of the product. Li et al. [13] and Tiwari et al. [14] modified slightly the same basic procedure as to obtain the purity of ferrate(VI) more than 99%.

Rubidium and cesium ferrate(VI) are also prepared using similar procedure. The alkaline earth metals (Strontium and Barium) ferrates(VI) are prepared by the reaction of metal chloride solution with a basic solution of potassium ferrate(VI) at 0 °C. In this process the CO<sub>2</sub> free water and inert atmosphere need to be prevailed. Rapid filtration gave the pure form of barium and strontium ferrate.

### 1.3 Characterization and estimation of Ferrate(VI)

The possible application of ferrate(VI) is greatly depends upon the characterization of the synthesized product and its purity. There are several analytical tools which enabled to characterize the ferrate(VI) efficiently. The analytical techniques used are FTIR, Mössbauer spectroscopy, UV/Vis spectroscopy, ICP titrimetric, electroanalytical methods and XRD analyses. The oxidation state of iron can be obtained with the help of Mössbauer spectroscopy, both for Fe(VI) and other iron species.

#### *Mössbauer Spectroscopic Analysis*

Sharma et al. [15] described the Mössbauer chemistry of different oxidation state of iron which can be given as:

Mössbauer spectroscopy, which is based on the recoilless nuclear resonance absorption/emission of gamma radiations, because of its low line width of gamma rays, makes it possible to hyperfine interaction of the nucleus with surrounding electrons. The electrons in surrounding will be measured precisely, which could provide the information on the structure of valance shell of the particular Mössbauer atom. This method is successfully applied when the conditions of recoilless nuclear resonance absorption/emission are met (Mössbauer effect), and, from this point of view, iron-57 is the best nuclide ever found. This is the reason Mössbauer Spectroscopy could become an important method in material science and especially unique for iron containing compounds. The oxidation state of iron can be learned from the Mössbauer isomer shift ( $\delta$ ) which is directly (and mostly) related to the s electron density within the nucleus. Absolute electron densities may not be measured, thus the isomer shift is a relative quantity. In <sup>57</sup>Fe Mössbauer Spectroscopy the most common reference material is metallic iron ( $\alpha$ -Fe). Due to the fact that the <sup>57</sup>Fe nucleus in its excited state (with nuclear spin  $I=3/2$ ) has a smaller radius than in its ground state ( $I=1/2$ ), an increasing electron density in the nucleus results in decreasing isomer shift. However, the valance shell of iron normally involves 3d-electrons which virtually screen the effect of the 3s electrons (the former being closer to the nucleus), and thus if the 3d electron density increases in the valance shell of iron (e.g., when Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup>) the 3s density will decrease in the nucleus, and one may observe an increasing isomer shift. Such considerations are of basic importance for the assignment of Mössbauer pattern to a particular oxidation state.

Similarly, the quadrupole splitting ( $\Delta$ ) is characteristic of the symmetry of electron density distribution around the nucleus, and it is mostly related to the 3d shell configuration of the Fe atom/ion. Completely filled or half filled 3d levels or 3d sublevels (i.e.,  $t_{2g}$  and  $e_g$ ) result in zero quadrupole splitting if nothing else perturbs the electron density distribution. The magnetic splitting caused by the magnetic field (B) is additional information from the Mössbauer spectrum, which can be crucial to identify a particular iron-containing phase. Figure 2 shows the 3d valence shell configuration of iron in its four most important oxidation states, using ligand field theory, together with the most common values of the Mössbauer parameters. The ligand field splitting corresponds to the most abundant cases i.e., octahedral for  $\text{Fe}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{IV}}$ , and tetrahedral for  $\text{Fe}^{\text{VI}}$ . Only high-spin cases (small ligand field splitting) are discussed.

3d shell configuration	Oxidation state	$\delta(\text{mm/s})$ Rel. to $\alpha\text{-Fe}$	$\Delta(\text{mm/s})$
	$\text{Fe}^{\text{II}}$	$\sim 1.1$	<i>large</i>
	$\text{Fe}^{\text{III}}$	$\sim 0.4$	<i>small or zero</i>
	$\text{Fe}^{\text{IV}}$	$\sim -0.2$	<i>small or zero</i>
	$\text{Fe}^{\text{VI}}$	$\sim -0.9$	<i>mostly zero</i>

Fig. 2. Schematic representation of the 3d shell configuration of iron in selected oxidation states with characteristic Mössbauer parameters. Isomer shifts are given at room temperature relative to  $\alpha\text{-Fe}$ , note that, the ligand field splitting corresponding to the most common octahedral coordination for  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{IV}}$  while it is tetrahedral for  $\text{Fe}^{\text{VI}}$  [15].

Among regular iron compounds,  $\text{Fe}^{\text{II}}$  has the highest isomer shift, and the  $3d^6$  configuration of the valence shell represents one more  $t_{2g}$  electron compared to  $3d^5$  of spherical symmetry, thus the quadrupole splitting is also large.

$\text{Fe}^{\text{III}}$  has only five 3d electrons, and therefore the isomer shift becomes smaller. Since the illustrated 3d splitting is only an idealized non-distorted case, the observed quadrupole splitting is very rarely zero, it is mostly below 1 mm/s and may even be larger. The distortion of the octahedron can be caused by the Jahn-Teller effect, lattice symmetry, neighboring charges, defects, etc.

$\text{Fe}^{\text{IV}}$  has only four 3d electrons, which is manifested in a further decrease of the isomer shift. The asymmetry of the 3d density distribution is somewhat similar to the case of  $\text{Fe}^{\text{III}}$  but the quadrupole splitting are surprisingly small or zero. It can be explained if one takes it into account that with increasing oxidation number, originally ionic states have a tendency to become covalent and the extra electron which would cause the asymmetry gets delocalized on the two  $e_g$  sublevels. Zero quadrupole splitting means that the perfect octahedral ligand environment is preserved.

$\text{Fe}^{\text{VI}}$  cannot exist as a  $\text{Fe}^{6+}$  ion, it should form an oxoanion,  $\text{FeO}_4^{2-}$ . Although ligand field approximation may not work in this case and MO theory would be more appropriate, the observed Mössbauer parameters fit in the tendency qualitatively very well, and very low isomer shift and zero quadrupole splitting found. Distortion of the rather stable tetrahedral  $\text{FeO}_4^{2-}$  anion is very rarely observed.

The characteristics of alkali and alkaline earth metal ferrate(VI) are shown in Table 2 [16] which obviously demonstrate that ferrate(VI) basic Mössbauer parameters *viz.*, isomer shift ( $\delta$ ), reflecting chemical state of iron(VI) changes in narrow limits i.e., 0.87 to 0.91  $\text{mm s}^{-1}$  (with respect to standard  $\alpha\text{-Fe}$ ). This indicates a weak influence of the outer ion on iron bonding in oxygen tetrahedron, which is main structural unit of all ferrates(VI).

Property	$\text{K}_3\text{Na}(\text{Fe}^{\text{VI}}\text{O}_4)_2$	$\text{K}_2\text{Fe}^{\text{VI}}\text{O}_4$	$\text{Rb}_2\text{Fe}^{\text{VI}}\text{O}_4$	$\text{Cs}_2\text{Fe}^{\text{VI}}\text{O}_4$	$\text{K}_2\text{Sr}(\text{Fe}^{\text{VI}}\text{O}_4)_2$	$\text{BaFe}^{\text{VI}}\text{O}_4$
$\Delta \text{ mm s}^{-1}$	-0.89 -0.88	-0.90 -0.88	-0.89	-0.87	-0.91	-0.90
$\Delta \text{ mm s}^{-1}$	0.21	0.0	0.0	0.0	0.14	0.16
H (T,K)	No magnetic ordering down to 4.2K	14.2±2.0 (2.8K) 14.7 (0.15K)	14.9±2.0 (2.8K)	15.1±2.0 (2.8K)	8.7 (2.0K) unresolved sextet	11.8±2.0 (2.8K)
T <sub>N</sub> (K)		3.6-4.2	2.8-4.2	4.2-6.0	~3	7.0-8.0

Table 2. Characteristics of ferrate(VI) [16]

IR spectra of potassium ferrate(VI) showed very characteristic peaks at the wave numbers 324 and 800  $\text{cm}^{-1}$  (*cf* Figure 3).

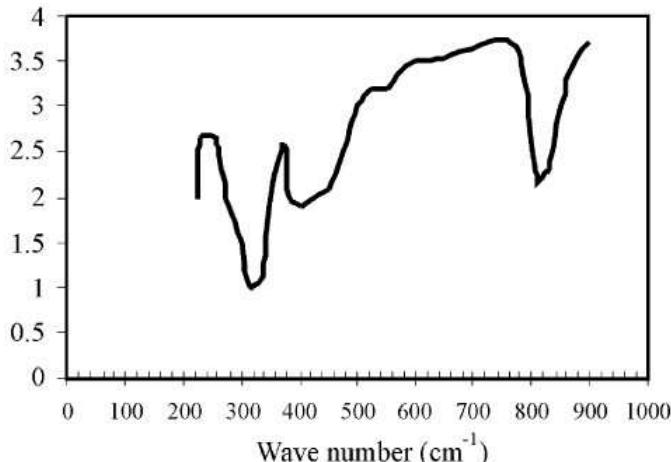


Fig. 3. IR spectrum of potassium ferrate [17].

Single crystal X-ray structural determination of  $K_2FeO_4$  was performed and suggested four equivalent oxygen atoms are covalently bonded to central iron atom in +6 oxidation state [18]. The tetrahedral structure was also confirmed by isotopic exchange study as performed in aqueous solutions [19]. The reliable simulated powder XRD patterns (ICSD file 2876 and 32756, [20]) and an experimental one (PDF file No. 25-652, [18]) as reference for the pure substance is available. Moreover, it was also proposed that Fe(VI) ions can have three resonance hybrid structures in aqueous solution as shown in figure (4) [21]. Of these three resonance structures in figure 4, the structures of '1' and '2' were suggested as main contributors to the resonance structures of Fe(VI) based on theoretical studies of metal oxide structures.

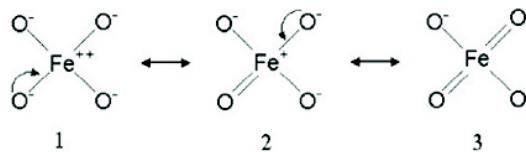


Fig. 4. Three resonance hybrid structures of Fe(VI) ion in an aqueous solution [21].

#### *Quantitative estimation of Ferrate(VI):*

Potassium ferrate  $K_2Fe^{VI}O_4$ , is most common and relatively easily synthesized ferrate salt. Moreover, the stability of this compound is fairly good under certain specified conditions. It is black-purple in color and remains stable in moisture excluded air exposure for longer period. In aqueous solution the ion  $Fe^{VI}O_4^{2-}$  is monomeric with a high degree of four 'covalent character' equivalent oxygen atoms [19,22]. Potassium ferrate is insoluble in commonly used organic solvents and can be suspended in benzene, ether, chloroform etc. without having rapid decomposition of compound [23]. Alcohols containing more than 20% water rapidly decomposed ferrate(VI) and resulted in the formation of aldehydes or ketones [23].

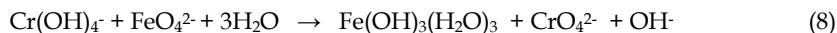
Ferrate(VI) can be easily analyzed quantitatively by the two different methods:

##### *i. Volumetric titration method, and (ii) UV-Visible Spectroscopic method*

The brief description of these methods is given below.

##### *i. Volumetric titration method*

This method is based on the strong oxidative power of the Fe(VI). In this method, the Fe(VI) was intended to oxidize the chromite salt (equation 8) and the oxidized chromate was titrated with the standard ferrous salt solution in an acidic medium, and sodium diphenylamine sulphonate was used as an indicator [24]. This method is useful to analyze the solutions containing low concentration of Ferrate(VI) ion in aqueous solutions.



Another method which is developed based on the oxidation of alkaline arsenite to arsenate using the ferrate(VI) in aqueous solution [25]. The chemical reactions took place given in equation (9). In this analytical method a known amount of ferrate(VI) was added to a standard alkaline solution, in which, the amount of arsenite was greater than that required for the reduction of ferrate(VI) ions. The excess arsenite was back titrated with standard bromate solution (equation (10)) or cerate solution equation (11). The equivalent of consumed bromate or cerate is then calculated and subsequently, the equivalent of ferrate was estimated.



It was further reported that although, the arsenite-bromate and arsenite-cerate methods shown equally satisfactory results but the back-titration with cerate is to be preferred comparing to the bromate titration, since the bromate titration is carried out while the solution is still hot and the acidity of the hydrochloric acid must be carefully controlled. However, arsenite-cerate method is not recommended for analyzing highly decomposed ferrate solutions (that contains large amounts of ferric hydroxide), as the o-phenanthroline end point is observed by the color of the excess ferric ions [2].

Further, it is to be noted that although the volumetric titration method is useful for quantitative determination of ferrate(VI), however, the decomposition of ferrate(VI) is rapid hence, a buffer solution of phosphate is required to maintain pH of the ferrate(VI) sample at 8, at which the self decomposition of ferrate(VI) is significantly suppressed and the results obtained are more reliable. Moreover, the samples wastes need to be stored and treated specifically owing to the existence of residual chromite in the wastes if the chromite-ferrous titration method was employed, or the presence of arsenite if arsenite-bromate/arsenite-cerate methods were used.

### *ii. UV-Visible Spectroscopic*

This is the most useful and robust method of ferrate(VI) quantification. In this method the aqueous solution of ferrate, which is red-violet in color and gives a characteristic absorption maxima at around 500 and 800 nm (cf Figure 5), can be used for its qualitative as well as quantitative estimation. Moreover, the aqueous solution of ferrate(VI) prepared in phosphate buffer between pH 9.0 and 10.5 are stable for hours makes it easy to obtain the spectral measurements at this pH.

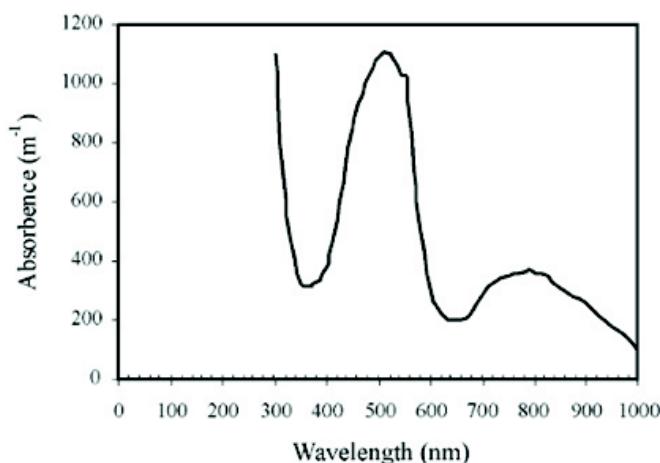


Fig. 5. UV-Vis spectrum of potassium ferrate(VI) [25].

The spectral measurements of  $\text{FeO}_4^{2-}$  were obtained in 0.0075M phosphate solution at different pH at 25 °C and it showed that the absorption spectra has a peak at ~510nm. Further, the accepted value of molar extinction coefficient for  $\text{FeO}_4^{2-}$  at pH 9.0 is 1150 M<sup>-1</sup>cm<sup>1</sup> [26-27,41].

An indirect method of ferrate(VI) determination was proposed using the spectrophotometric determination [28]. ABTS (2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonate) interacts with Fe(VI) and gives a green radical cation of ABTS ( $\text{ABTS}^{\cdot+}$ ) which showed a characteristic absorption maxima at 415 nm. This was observed that the increase in absorbance at 415 nm for the radical ABTS<sup>·+</sup> is linear with the increase in Fe(VI) concentration (0.03 to 35 μM) in the acetate/phosphate buffer solution at pH 4.3. The molar extinction coefficient was calculated and found to be  $3.40 \pm 0.05 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .

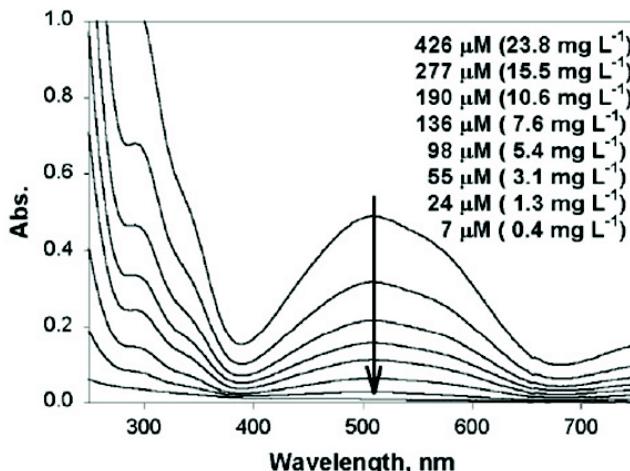
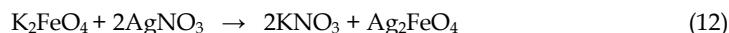


Fig. 6. UV-Vis absorption spectrum of Fe(VI) in aqueous solution as a function of its concentration, pH = 9.2, 25 mM phosphate buffer [27].

In addition to above said two methods, reports included the chemical precipitation method of its estimation [29]. In a small glass-stopped bottle, 10 mL of potassium ferrate(VI) solution was mixed with 20 mL of 0.1 M silver nitrate solution (equation (12)) and the resulting precipitate was filtered, which contained the silver ferrate and its color was black with a pink reflection, indicating the presence of potassium ferrate(VI) in the solution. After heating, the precipitate dissociated into silver oxide, ferric oxide and oxygen (equation (13)).



#### 1.4 Stability and speciation of Ferrate(VI)

The stability of ferrate(VI) of its aqueous solutions depends on several factors *viz.*, ferrate(VI) concentration, temperature of the solution, co-existing ions, pH etc. [30]. The dilute solutions of Fe(VI) seems to be more stable than concentrated [31]. The solution of 0.025M Fe(VI) will remain 89% even after the 60 min but if the initial concentration of Fe(VI) was increased to 0.03 M, almost all the ferrate ions will get decomposed within the same period of time i.e., 60 min. Other reports also demonstrated that a 0.01M potassium ferrate

solution decomposed to 79.5% over a period of 2.5 h, while a 0.0019M potassium ferrate solution decreased to only 37.4% after 3 h and 50 min at 25 °C [32].

The stability of  $K_2FeO_4$  in 10 M KOH is increased from hours to week if no  $Ni^{2+}$  and  $Co^{2+}$  impurities are present (< 1 $\mu$ M) [33]. However, nitrate salts of  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and other salts including  $K_2Zn(OH)_4$ ,  $KIO_4$ ,  $K_2B_4O_9$ ,  $K_3PO_4$ ,  $Na_2P_2O_7$ ,  $Na_2SiF_6$ ,  $Na_2SiO_3$ ,  $Na_2MoO_4$  and  $Na_2WO_4$  have no affect on the stability of  $K_2FeO_4$  [33]. A 0.5 M  $K_2FeO_4$  solution, containing KCl,  $KNO_3$ , NaCl and FeOOH was studied to observe the ferrate(VI) stability in presence of these salts. It was found that the ferrate(VI) decomposed rapidly in the initial stage and appeared relatively stable at low ferrate concentrations when KCl and  $KNO_3$  were present [31]. Phosphate was shown to retard the ferrate(VI) decomposition.

The spontaneous decomposition of ferrate(VI) in aqueous solutions was reported to be increased significantly with decreasing the solution pH. Figure 7 obtained with using the 1 mM solution of  $K_2FeO_4$  in aqueous solution showed that at pH ~5, just after 7 min, the Fe(VI) was decomposed completely, however, at pH ~9 and ~10, it was fairly stable even after elapsed time of 20 min [34]. Other studies, conducted with 2h test period, the concentration of potassium ferrate slightly decreased when it was in 6M KOH, but decreased rapidly when it was in 3M KOH. The ferrate solution prepared with buffer solution at pH 8 was more stable than that prepared at pH 7 [31]; 49% of the original potassium ferrate remained after 8 h when the pH was 7, and 71.4% of that remained after 10 h when the pH was 8.

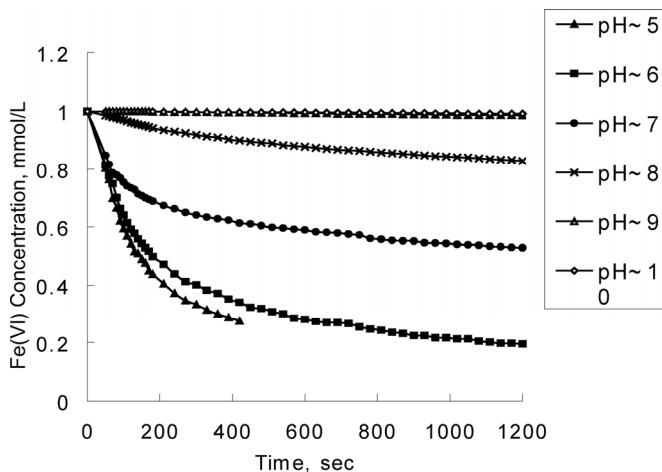


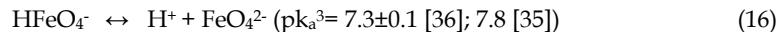
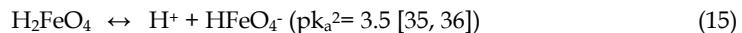
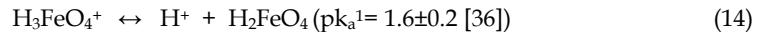
Fig. 7. The change of the Fe(VI) concentration as a function of time at various pH values [Initial concentration of Fe(VI): 1 mM] [34].

Temperature dependence data showed that ferrate(VI) solutions are relatively stable at low temperature conditions (0.5 °C) [32]. The 0.01 M solution of Fe(VI) was reduced by 10% at a constant temperature of 25 °C and almost unchanged at 0.5 °C for a period of 2 h.

#### Speciation and Decomposition of Fe(VI)

The presence of at least two unstable protonated form of Fe(VI) i.e.,  $H_2FeO_4$  and  $HFeO_4^-$  was reported in 0.2 M phosphate buffer solutions at 25 °C [35]. However, a similar study in 0.025 M phosphate/acetate buffers at 23 °C showed three protonated forms of Fe(VI)

(equations (14-16)) [36]. The  $pK_a$  for  $HFeO_4^-/FeO_4^{2-}$  (equation (16)) were also found different in the two different studies. The discrepancy in  $pK_a^3$  was attributed to the difference in the buffer concentrations used.



These  $pK_a$  values indicated that the presence of four different ferrate(VI) species in the entire pH range (Figure 8). Figure 8 clearly indicated that  $HFeO_4^-$  and  $FeO_4^{2-}$  species are predominant species in neutral and alkaline solutions, at which the Fe(VI) was known to be relatively stable towards its spontaneous dissociation [37].

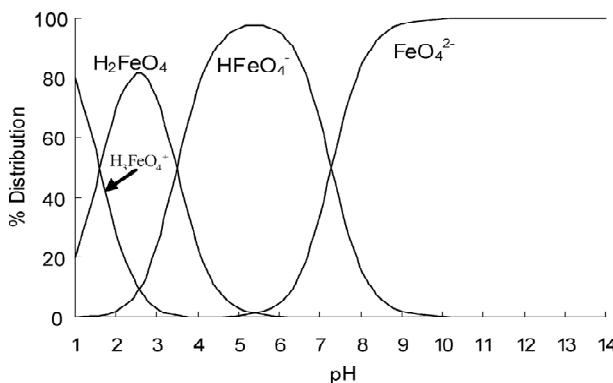
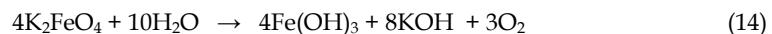
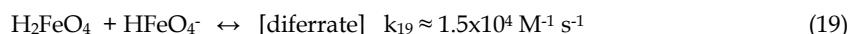
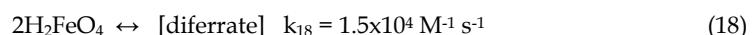
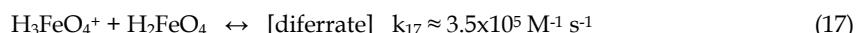
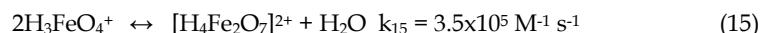


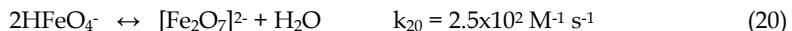
Fig. 8. Speciation of ferrate(VI) in aqueous solutions [Concentration of Fe(VI): 1mM] [34].

The ferrate salts when dissolved in water, oxygen is evolved and ferric hydroxide is precipitated (equation (14)).



The rate of decomposition of ferrate(VI) has already seen that it is strongly pH dependent. The lowest rate of decomposition was occurred at pH higher than ~9-10, while it increased significantly at lower pH values [35,38]. The reaction kinetics followed second-order below pH 9.0, while first order above pH 10.0 [37]. The decomposition of ferrate(VI) hence, described by the following equilibrium and kinetic models [36]:





Reactions clearly showed that the forward reactions (15) to (20) (except reaction (16)) are relatively slow steps hence, could be the rate determining steps. The rate constants were then calculated for the self decomposition of Fe(VI), which is to be second order reactions. The second order rate constants for the decomposition of Ferrate(VI) to iron(II) in 5 mM phosphate/acetate buffers are obtained and shown in figure 9 [36].

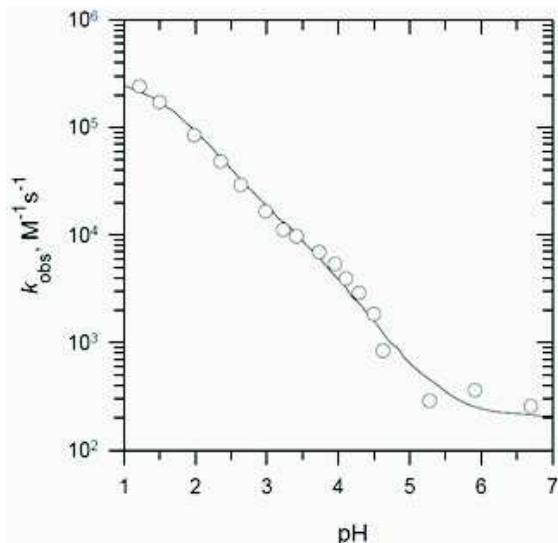


Fig. 9. The second-order rate constants for the decay of ferrate(VI) to iron(II) in 5 mM (phosphate/acetate) buffers [36].

### 1.5 Basic principle of Fe(VI) treatment in the wastewater

Ferrate(VI) applications in general lies in different area of research *viz.*, environmental remediation (i.e., oxidant, coagulant, disinfectant, antifouling oxidant etc.), cathode material for batteries (i.e., Super iron battery); Green synthesis oxidant (i.e., selective organic synthesis); and source of hypervalent iron (i.e., several biochemical research as to use more powerful oxidant) etc. Most of these applications are based on the reactivity or the oxidizing capacity of the ferrate(VI). The oxidizing power in general increases from chromium to manganese to iron (table 3). The closure observation showed that the reduction potential of Cr(VI)/Cr(III) and Mn(VII)/Mn(IV) were significantly lower than that of Fe(VI)/Fe(III). Even the commonly used oxidant *viz.*, ozone, hydrogen peroxide, hypochlorite, chlorine, perchlorate etc. are also possessed comparably less reduction potential [Table 3]. Moreover, the oxidation process usually occurred with Fe(VI), completed in shorter periods than oxidations carried out by permanganate or chromate. Therefore, these properties makes ferrate(VI) a potential chemical for the various applications, in particular to its oxidative properties.

In other words, taking Fe(VI) in aqueous medium it decomposes to Fe(III) and produces nascent oxygen (reaction (14)) which makes it highly reactive hence, could be applied for the treatment of wastewaters. This is the basic principle lies with ferrate(VI) application particularly for the treatment of wastewaters since, it degraded the degradable organic or

even inorganic impurities. Similarly, it could be potentially applied towards the disinfection of the water bodies as it may serve as one of the promising chemical to destroy/kill various pathogens/bacteria/viruses. Moreover, the reaction (14) also indicated that, it produces Fe(III) after its reduction which termed to be remarkably a good coagulant/flocculants hence, in the later stage it can serve as a coagulant/flocculants which may be able to remove the non-degradable impurities. Keeping in view with such basic properties of Ferrate(VI), it was first used by the Murmann and Robinson as a multi-purpose water treatment chemical for the oxidation, coagulation and disinfection of water [39]. Presently, it has already been assessed and successfully employed for the treatment of variety of wastewaters contaminated with several organic and inorganic pollutants along with as a potential disinfectant. Applications of ferrate(VI) in the waste waters treatment was intended with fast effective and less sludge producing method hence, in recent past it attracted an enhanced attention for its wider application in such treatment techniques.

Oxidant	Reaction	$E^0, V$
Chlorine	$\text{Cl}_2(\text{g}) + 2\text{e}^- \leftrightarrow 2\text{Cl}^-$ $\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{Cl}^- + 2\text{OH}^-$	1.358 0.841
Hypochlorite	$\text{HClO} + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O}$	1.482
Chlorine dioxide	$\text{ClO}_2(\text{aq}) + \text{e}^- \leftrightarrow \text{ClO}_2^-$	0.954
Perchlorate	$\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \leftrightarrow \text{Cl}^- + 4\text{H}_2\text{O}$	1.389
Ozone	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{O}_2 + 2\text{H}_2\text{O}$	2.076
Hydrogen peroxide	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$	1.776
Dissolved oxygen	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$	1.229
Permanganate	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \leftrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.679 1.507
Chromate	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \leftrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
Ferrate(VI)	$\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \leftrightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$ $\text{FeO}_4^{2-} + 8\text{H}_2\text{O} + 3\text{e}^- \leftrightarrow \text{Fe(OH)}_3 + 8\text{H}_2\text{O}$	2.20 0.70

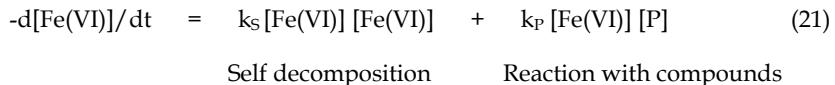
Table 3. Redox potential for the different oxidants used in water and wastewater treatment

### 1.6 Fe(VI): a green chemical

The application of ferrate(VI) in various applications of applied sciences is associated with a non-toxic by-products which exaggerates its applications in different purposes. In particular, the ferrate(VI) treatment technology for the treatment of wastewaters as described earlier (equation (14)) associated with the Fe(III) by-product which is rendered as non-toxic chemical hence, the ferrate(VI) treatment is absolutely free from the toxic by-products. Therefore, the entire treatment is known as the 'Green-Treatment' and ferrate(VI) is termed as a 'Green-Chemical'. Based on its unique multifunctional properties as well possessed with green nature it may be one of the chemical of next generation and could be used widely in future for the remediation of the aquatic environment. Moreover, Ferrate(VI) is an emerging water-treatment disinfectant and coagulant, which can address the stringent water standards maintained by the agencies. The concerns of disinfectant by-products (DBPs) associated with currently used chemicals such as free chlorine, chloramines, and ozone can be addressed using Fe(VI). Additionally, like ozone, Fe(VI) does not react with bromide ion; so carcinogenic bromate ion is not produced in the treatment of bromide containing water [40].

## 2. Fe(VI) treatment in the degradation of degradable pollutants

Because of its strong oxidizing capacity, ferrate(VI) employed as potential chemical to degrade the variety of inorganic and organic impurities in aqueous solutions. The important aspects of such degradation is the reactivity of the Ferrate(VI), the mechanism involved in the degradation process and the kinetics with possible stoichiometry are the point of discussion. These parameters are useful inputs for the technology development and further implication of this technique. These are well discussed in the following sections and summarized in the proceeding tables and figures. The reaction of Fe(VI) was categorized into two pathways, (i) its self decomposition (i.e.,  $k_S[Fe(VI)][Fe(VI)]$ , reactions (15-20), except (16)), and (ii) reaction with other compounds (i.e.,  $k_P[Fe(VI)][P]$ ), which can be well conceptualized by the following reaction of rate expression:



The rate of reaction because of its self-decomposition can be minimized under the certain conditions *viz.*, at higher pH values, using phosphate buffers or even while studying the kinetic studies of unknown compounds, this may be subtracted as a blank run. The second rate determining step is an important factor which determines the rate of decomposition of compounds. This is of second order reaction and the rate constants for such second order reactions are evaluated and discussed. Moreover, in excess of Fe(VI) concentration, and with ignoring the self-decomposition of ferrate(VI) the above reaction may be treated as pseudo first-order rate equation and the rate constants may be evaluated.

### 2.1 Application of Fe(VI) for organic pollutants

Ferrate(VI) showed significantly reactive towards a variety of aliphatic and aromatic organic compounds. The application of Fe(VI) was studied including the alcohols, carboxylic compounds, amino acids, phenol, 1,2-Diols, organic nitrogen and sulphur containing compounds, aliphatic sulphur, nitrosamines, hydrazine etc. The degradation of these compounds with Fe(VI) was reported to be relatively fast and the increase of Fe(VI) dose favored the decomposition of these compounds. The reaction mechanism proposed with Fe(VI) was one-electron and two-electron transfer reactions to be associated with the degradation process for these organics. Bielski and Thomas [41] first proposed the one electron reduction of Fe(VI) to Fe(V) by its reaction with hydrated electron ( $e_{aq^-}$ ), (reaction (22)). Further, studies showed that Fe(VI) could be reduced to Fe(V) through one electron transfer by its reaction to organic radical compounds, which was well-known one-electron reductants (reaction (23)) and reaffirmed with their pulse radiolysis and fast spectroscopic results [42-44].

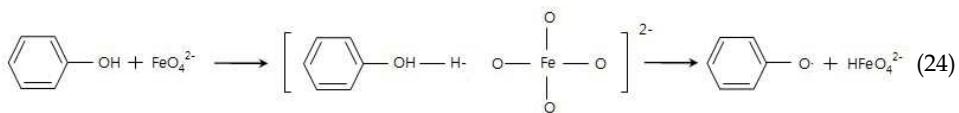


Similarly, the reaction of phenol with Fe(VI) was demonstrated with the phenoxy radical formation through hydrogen abstraction pathway (one-electron transfer), based on their reaction products analysis [45]. It was further, supported by the EPR studies, showed that

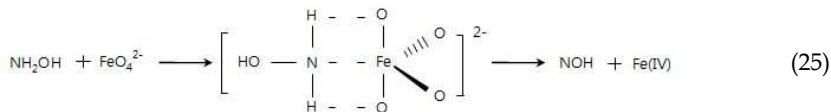
Organic Compound	pH	Rate constant $k_p$ (M <sup>-1</sup> s <sup>1</sup> )	t <sub>1/2</sub>	Reference
Aniline	9.0	1.3x10 <sup>4</sup>	0.15s	[50]
Acetaldehyde	8.0	4.0x10 <sup>-1</sup>	1.39h	[35]
Benzenesulfinate	9.0	1.4x10 <sup>2</sup>	14.3s	[51]
Chloral	8.0	6.0x10 <sup>0</sup>	5.55min	[35]
Cysteine	12.4	7.6x10 <sup>2</sup>	2.6s	[52]
Cystine	12.4	1.2x10 <sup>2</sup>	16.7s	[52]
Diethylamine	8.0	7.0x10 <sup>-1</sup>	47.6min	[35]
Diethylsulfide	8.0	1.0x10 <sup>2</sup>	20.0s	[35]
Dimethylamine	8.0	2.0x10 <sup>2</sup>	10.0s	[35]
Dimethylsulphoxide	8.0	1.0x10 <sup>0</sup>	33.3min	[35]
Dimethylglycine	8.0	2.5x10 <sup>0</sup>	13.3min	[35]
Ethylene glycol	8.0	4.0x10 <sup>-2</sup>	13.9h	[35]
Ethyl alcohol	8.0	8.0x10 <sup>-2</sup>	6.94h	[35]
Formic acid	8.0	4.0x10 <sup>-1</sup>	1.39h	[35]
Formaldehyde	8.0	5.0x10 <sup>-1</sup>	1.11h	[35]
Glycine	8.0	1.0x10 <sup>2</sup>	20.0s	[35]
Glycolaldehyde	8.0	3.0x10 <sup>0</sup>	11.1 min	[35]
Glycolic acid	8.0	4.0x10 <sup>-1</sup>	1.39h	[35]
Glyoxal	8.0	3.0x10 <sup>2</sup>	6.7s	[35]
Glyoxalic acid	8.0	7.0x10 <sup>2</sup>	2.9s	[35]
p-Hydroquinone	9.0	2.0x10 <sup>5</sup>	10.0ms	[42]
Iminodiacetic acid	8.0	1.0x10 <sup>2</sup>	20.0s	[35]
Isopropyl alcohol	8.0	6.0x10 <sup>-2</sup>	9.26h	[35]
2-Mercaptobenzoic acid	10.0	2.5x10 <sup>4</sup>	89.0ms	[53]
2-Mercaptoethanesulfonic acid	9.0	3.0x10 <sup>4</sup>	66.7ms	[53]
Mercaptopropionic acid	9.0	1.3x10 <sup>4</sup>	0.15s	[54]
Methylhydrazine	9.0	9.8x10 <sup>3</sup>	0.20s	[47]
Methionine	9.0	1.3x10 <sup>2</sup>	15.4s	[52]
Methylamine	8.0	4.0x10 <sup>1</sup>	50.0s	[35]
Methyl alcohol	8.0	3.0x10 <sup>-2</sup>	18.5h	[35]
N-methyliminodiacetic acid	8.0	2.0x10 <sup>0</sup>	16.7min	[35]
Nitroacetic acid	8.0	2.0x10 <sup>0</sup>	16.7min	[35]
Neopentyl alcohol	8.0	1.0x10 <sup>-1</sup>	5.55h	[35]
Oxalic acid	8.0	1.0x10 <sup>-1</sup>	5.55h	[35]
Phenol	9.0	8.0x10 <sup>1</sup>	25.0s	[35]
p-Hydroquinone	9.0	2.0x10 <sup>5</sup>	10.0s	[42]
p-Toluidine	9.0	1.3x10 <sup>3</sup>	1.5s	[50]
p-Aminobenzoic acid	9.0	4.3x10 <sup>1</sup>	46.9s	[50]
p-Nitroaniline	9.0	3.0x10 <sup>1</sup>	1.10min	[50]
Sarcosine	8.0	1.2x10 <sup>2</sup>	16.7s	[35]
Thiodietanol	8.0	1.0x10 <sup>2</sup>	20.0s	[35]
Thioxane	9.0	5.8x10 <sup>1</sup>	34.5s	[55]
Trimethylaldehyde	8.0	2.0x10 <sup>0</sup>	16.7min	[35]

Table 4. Fe(VI) oxidation of various organic compounds

the oxidation of phenol by Fe(VI) proceeded through an intermediate radical species which was presumed as phenoxy radical (reaction (24)) [46].



Further, the two-electron transfer mechanism of Fe(VI) was proposed for the degradation of several nitrogen containing compounds [47-49]. The oxidation of hydroxylamine was suggested to occur by concerted two hydrogen abstraction mechanism via the adduct formation between Fe and N atom of both reactants (reaction (25)) [49]. This argument was based on their several experimental results, including the stoichiometric, kinetic and products analysis of the reaction. The results of one-electron *viz.*, ascorbates, amino acids, esters, phenol, thiourea, thioacetamide etc. or two electron *viz.*, hydrazine, methylhydrazine, thiosulfate, benzenesulfinate, methionine, alcohols, thiol compounds, 1,4-thioxane, hydroxylamines, aniline etc. processes are compiled elsewhere [27].



The second order reaction rate constants i.e.,  $k_p$  (equation (21)) for the degradation of several organic pollutants in aqueous solutions are obtained and compiled in Table 4. Since, reaction rate is dependent to the solution pH hence, the pH was also specified. This table also includes the half-life period of reaction. These results inferred that most of the studies conducted at relatively higher pH condition where the Fe(VI) is stable. Moreover, the dominant species of the Fe(VI) are the  $\text{FeO}_4^{2-}$  and  $\text{HFeO}_4^{2-}$  (figure 8). The reaction rate constants are high enough, whereas the half life period is relatively low (except few cases) suggesting fast and effective degradation reaction occurred with ferrate(VI).

## 2.2 Application of Fe(VI) for inorganic pollutants

The oxidation of inorganic pollutants present in the aquatic environment is a major concern for several environmental remediation strategies. The possible impurities are free or metal complexed species including the heavy metal toxic ions, cyanide, dissolved ammonia, hydroxylamines, hydrogen sulphide, thiourea, thioacetamide etc. These potential contaminants are treated with Fe(VI). The mechanism of oxidation of inorganic compounds with ferrate(VI) was suggested to be one and two-electron process. Compounds like iodides, cyanides, sulfite etc. demonstrated to be one electron process whereas, the oxy compounds of arsenic, selenium, nitrogen and sulphur are possessed with the two-electron mechanism while these are reacted/degraded with Fe(VI).

The reactions of ferrate(VI) with a series of inorganic compounds such as iodide, cyanide, superoxide, sulfide, hydrazine, ammonia, azide and oxy-compounds of nitrogen, sulphur, selenium and arsenite possessed with seconds-order kinetics [38,47,49,51,57-65]. In general, similar to the organic compounds the reaction with inorganic compounds (P) may be demonstrated as equation (26):

$$-\frac{d[\text{Fe(VI)}]}{dt} = k_p [\text{Fe(VI)}][\text{P}] \quad (26)$$

where  $k_P$  is the second-order rate constant for the reaction. It was found that the reactions of ferrate(VI) with cadmium(II)cyanide ( $\text{Cd}(\text{CN})_4^{2-}$ ), zinc(II)cyanide ( $\text{Zn}(\text{CN})_4^{2-}$ ), and selenite ( $\text{SeO}_3^{2-}$ ) showed the following rate equations (27 and 28) [56,66-67]. The order of  $1/2$  was found with respect to the concentrations of Cd(II) and Zn(II) cyanides (equation (27)). This is different from the second-order rate law observed for the reaction of Fe(VI) with other cyanides ( $\text{CN}^-$ ,  $\text{SCN}^-$ ,  $\text{Cu}(\text{CN})_4^{3-}$  and  $\text{Ni}(\text{CN})_3^-$ ) [61,64,67-68]

$$-\frac{d[\text{Fe(VI)}]}{dt} = k_P[\text{Fe(VI)}][\text{M}(\text{CN})_4^{2-}]^{0.5} \text{ where M= Cd(II), Zn(II)} \quad (27)$$

The reaction of ferrate(VI) and selenite possessed with first and second-order selenite concentrations dependence terms in the rate law (equation (28)) [56].

$$-\frac{d[\text{Fe(VI)}]}{dt} = k_P[\text{Fe(VI)}][\text{SeO}_3^{2-}] + k_2 [\text{Fe(VI)}][\text{SeO}_3^{2-}]^2 \quad (28)$$

where  $k_2$  is the third order rate constant.

Recently, the rate constants estimated for various inorganic compounds are tabulated in the Table 5 [69]. Moreover, the stoichiometry and the products obtained by oxidation of Fe(VI) are compiled and returned in Table 6 [69,59].

Compound (P)	Rate constant $k_P$ ( $\text{M}^{-1}\text{s}^{-1}$ )	
	$\text{HFeO}_4^- + \text{P}$	$\text{FeO}_4^{2-} + \text{P}$
Iodide ( $\text{I}^-$ )	$1.06 \pm 0.07 \times 10^4$	-
Cyanide ( $\text{HCN} + \text{CN}^-$ )	$1.76 \pm 0.07 \times 10^2$	$4.45 \pm 0.08 \times 10^{2a}$
Thiocyanate, $\text{SCN}^-$	$3.25 \pm 0.20 \times 10^3$	-
Iron(II)tetracyanide, $\text{Fe}(\text{CN})_4^{2-}$	$3.00 \times 10^3$	-
Copper(I)tetracyanide, $\text{Cu}(\text{CN})_4^{3-}$	$5.33 \pm 0.71 \times 10^7$	$2.51 \pm 1.42 \times 10^4$
Nickel(II)tetracyanide, $\text{Ni}(\text{CN})_4^{2-}$	$1.19 \pm 0.12 \times 10^3$	$1.50 \pm 0.15 \times 10^0$
Cadmium(II)tetracyanide, $\text{Cd}(\text{CN})_4^{2-}$	$6.71 \pm 0.17 \times 10^2$	$2.26 \pm 1.47 \times 10^{-1b}$
Zinc(II) tetracyanide, $\text{Zn}(\text{CN})_4^{2-}$	$4.05 \pm 0.20 \times 10^2$	$2.39 \pm 0.14 \times 10^{-1b}$
Hydrogen sulfide, $\text{H}_2\text{S}$	$2.37 \pm 0.70 \times 10^7$	$1.52 \pm 0.52 \times 10^3$
Bisulfite, $\text{SO}_3^{2-}$	$1.31 \pm 0.04 \times 10^5$	-
Thiosulfate, $\text{S}_2\text{O}_3^{2-}$	$4.14 \pm 0.19 \times 10^4$	-
Dithionite, $\text{S}_2\text{O}_4^{2-}$	$5.59 \pm 0.53 \times 10^7$	$2.84 \pm 0.25 \times 10^4$
Trithionate, $\text{S}_3\text{O}_6^{2-}$	$3.31 \pm 0.60 \times 10^1$	$4.41 \pm 1.23 \times 10^{-1}$
Pentathionate, $\text{S}_5\text{O}_6^{2-}$	$1.10 \pm 0.10 \times 10^2$	-
Hydroxylamine, $\text{NH}_2\text{OH}$	$6.47 \pm 1.49 \times 10^5$	-
Hydrazine, $\text{N}_2\text{H}_4$	$1.76 \pm 0.02 \times 10^6$	$6.76 \pm 0.05 \times 10^1$
Azide, $\text{N}_3^-$	$8.54 \pm 0.20 \times 10^{6c}$	-
Nitrite, $\text{NO}_2^-$	$7.56 \pm 0.11 \times 10^3$	-
Selenite, $\text{SeO}_3^{2-}$	$3.98 \pm 0.20 \times 10^2$	-
Arsenite, $\text{As(OH)}^3$	$2.56 \times 10^3$	-

<sup>a</sup>HCN ; <sup>b</sup>M<sup>0.5</sup>s<sup>-1</sup> ; <sup>c</sup>N<sub>3</sub>H<sup>+</sup>

Table 5. Rate constants for the oxidation of inorganic compounds by Fe(VI) [1,69]

Similarly, the degradation of thiourea and thioacetamide was studied [70-71] and it was proposed that thiourea and thioacetamide are to be converted into sulphate at pH 9.0 using the ferrate(VI). The stoichiometric ratios of Fe(VI) and thiourea and thioacetamide was found to be  $1:0.38 \pm 0.02$  (*cf.* Figures 10 and 11). Moreover, the proposed reaction was suggested as equations (29) and (30).

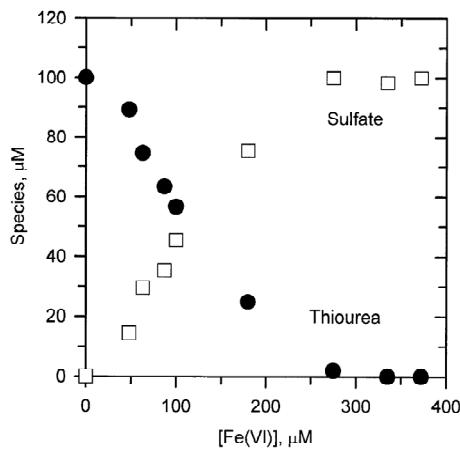
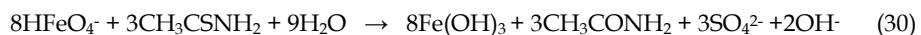


Fig. 10. A plot of thiourea consumption and sulfate formation versus [Fe(VI)] at pH 9.0 (Initial Thiourea:  $100 \times 10^{-6}$  M; [Fe(VI)] = 50-375  $\mu\text{M}$ ) [70].

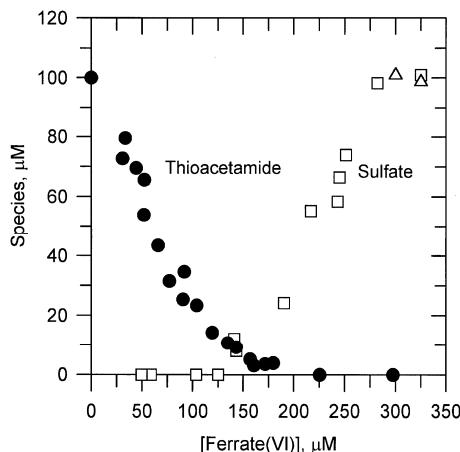


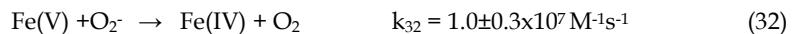
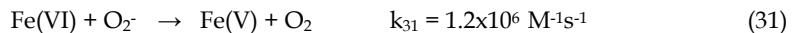
Fig. 11. A plot of thioacetamide consumption and sulfate formation versus [Fe(VI)] at pH 9.0 ( $\Delta$ -acetamide) (Initial Thioacetamide:  $100 \times 10^{-6}$  M; [Fe(VI)] = 50-375  $\mu\text{M}$ ) [71].

Pollutant (P)	pH	Stoichiometric equation
Cyanide ( $\text{HCN} + \text{CN}^-$ )	9.0	$2\text{HFeO}_4^- + 3\text{CN}^- + \text{OH}^- \rightarrow 2\text{Fe(OH)}_3 + 3\text{NCO}^-$ [61]
Thiocyanate, $\text{SCN}^-$	9.0	$4\text{HFeO}_4^- + \text{SCN}^- + 5\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + \text{NCO}^- + \text{SO}_4^{2-} + \text{O}_2 + 2\text{OH}^-$ [64]
Iron(II)tetracyanide, $\text{Fe}(\text{CN})_4^{2-}$	9.0	$\text{HFeO}_4^- + 3\text{Fe}(\text{CN})_6^{2-} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{Fe}(\text{CN})_6^{3-} + 4\text{OH}^-$ [58]
Copper(I)tetracyanide, $\text{Cu}(\text{CN})_4^{3-}$	9.0	$\text{HFeO}_4^- + \text{Cu}(\text{CN})_4^{3-} + 8\text{H}_2\text{O} \rightarrow 5\text{Fe(OH)}_3 + 4\text{NCO}^- + \text{Cu}^{2+} + 6\text{OH}^- + 3/2 \text{O}_2$ [63]
Nickel(II)tetracyanide, $\text{Ni}(\text{CN})_4^{2-}$	9.0	$4\text{HFeO}_4^- + \text{Ni}(\text{CN})_4^{2-} + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 4\text{NCO}^- + \text{Ni}^{2+} + 4\text{OH}^- + \text{O}_2$ [66]
Cadmium(II)tetracyanide, $\text{Cd}(\text{CN})_4^{2-}$	9.0	$4\text{HFeO}_4^- + \text{Cd}(\text{CN})_4^{2-} + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 4\text{NCO}^- + \text{Cd}^{2+} + 4\text{OH}^- + \text{O}_2$ [66]
Zinc(II)cyanide, $\text{Zn}(\text{CN})_4^{2-}$	9.0	$4\text{FeO}_4^- + \text{Zn}(\text{CN})_4^{2-} + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 4\text{NCO}^- + \text{Zn}^{2+} + 4\text{OH}^- + \text{O}_2$ [67]
Hydroxylamine, $\text{NH}_2\text{OH}$	Alkaline	$\text{HFeO}_4^- + 2\text{NH}_2\text{OH} \rightarrow \text{Fe(OH)}_2 + \text{N}_2\text{O} + \text{OH}^- + 2\text{H}_2\text{O}$ [49]
Hydrazine, $\text{N}_2\text{H}_4$	Alkaline	$\text{HFeO}_4^- + \text{N}_2\text{H}_4 \rightarrow \text{Fe(OH)}_2 + \text{N}_2 + \text{OH}^- + \text{H}_2\text{O}$ [47]
Azide, $\text{N}_3^-$	Alkaline	$\text{HFeO}_4^- + \text{N}_3^- + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + \text{N}_2 + \text{N}_2\text{O} + 2\text{OH}^-$
Nitrite, $\text{NO}_2^-$	Alkaline	$\text{HFeO}_4^- + 3\text{NO}_2^- + 3\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3\text{NO}_3^- + 2\text{OH}^-$ [61]
Hydrogen Sulphide, $\text{H}_2\text{S}$	7.0 9.0-11.3	$3\text{HFeO}_4^- + 4\text{H}_2\text{S} + 7\text{H}^+ \rightarrow 2\text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-} + 2\text{S(s)} + 9\text{H}_2\text{O}$ $8\text{HFeO}_4^- + 3\text{H}_2\text{S} + 6\text{H}_2\text{O} \rightarrow 8\text{Fe(OH)}_3 + 3\text{SO}_4^{2-} + 2\text{OH}^-$ [60]
Bisulfite, $\text{SO}_3^{2-}$	Alkaline	$2\text{HFeO}_4^- + 3\text{SO}_3^{2-} + 3\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3\text{SO}_4^{2-} + 2\text{OH}^-$
Thiosulfate, $\text{S}_2\text{O}_3^{2-}$	7.5-11.0	$2\text{HFeO}_4^- + \text{S}_2\text{O}_3^{2-} + 2\text{OH}^- + 3\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 6\text{SO}_3^{2-}$ [51]
Dithionite, $\text{S}_2\text{O}_4^{2-}$	Alkaline	$2\text{HFeO}_4^- + 3\text{S}_2\text{O}_4^{2-} + 4\text{OH}^- \rightarrow 2\text{Fe(OH)}_3 = 6\text{SO}_3^{2-}$
Trithionate, $\text{S}_3\text{O}_6^{2-}$	Alkaline	$10\text{HFeO}_4^- + 6\text{S}_3\text{O}_6^{2-} + 12\text{H}_2\text{O} \rightarrow 10\text{Fe(OH)}_3 + 9\text{S}_2\text{O}_6^{2-} + 4\text{OH}^-$
Pentathionate, $\text{S}_5\text{O}_6^{2-}$	Alkaline	$10\text{HFeO}_4^- + 2\text{S}_5\text{O}_6^{2-} + 12\text{H}_2\text{O} \rightarrow 10\text{Fe(OH)}_3 + 5\text{S}_2\text{O}_6^{2-} + 4\text{OH}^-$
Selenite, $\text{SeO}_3^{2-}$	Alkaline	$2\text{HFeO}_4^- + 3\text{SeO}_2^{2-} + 3\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3\text{SeO}_4^{2-} + 2\text{OH}^-$ [56]
Arsenite, $\text{As}(\text{OH})_3$	9.0	$2\text{HFeO}_4^- + 3\text{As}(\text{OH})_3 + 7\text{OH}^- \rightarrow 2\text{Fe(OH)}_3 + 3\text{AsO}_4^{3-} + 6\text{H}_2\text{O}$ [65]

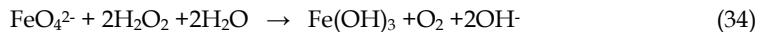
Table 6. Stoichiometry and product of oxidation of inorganic compounds by ferrate(VI) [1,59]

### *Fe(VI) Reaction with Superoxide and Hydrogen Peroxide*

Superoxides interacted with Fe(VI) and the second order rate equation demonstrated the reaction mechanism [72]. Further, the stoichiometry of the reactions ( $[Fe(VI)]/[O_2^-]$ ) were found to be 1:2 and 1:1 at pH 10.0 and 8.2, respectively. Reactions (31 – 33) are suggested for the observed stoichiometry:



The stoichiometries of the reactions between ferrate(VI) with hydrogen peroxide at pH 9.0 was presented (reaction (34)) [19].



The oxygen produced in this reaction showed the same isotopic composition as in the  $H_2O_2$ , which suggested that the O-O bond was retained in the oxidation of  $H_2O_2$  by ferrate(VI) [19].

### **2.3 Endocrine disrupting compounds degradation using Fe(VI)**

Endocrine disrupting compounds (EDCs) are chemicals with the potential to elicit negative effects on the endocrine systems of humans and wildlife. Various synthetic and natural compounds are known to induce estrogen-like responses; including pharmaceuticals, pesticides, industrial chemicals and heavy metals [73]. The US environmental protection agency (USEPA) defines an EDC as: "An exogenous agent that interferes with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behaviour" [74].

The broad class of EDCs chemicals includes natural estrogens such as estrone (E1),  $17\beta$ -estradiol (E2), and estriol (E3); natural androgens such as testosterone (T), dihydrotestosterone (DHT), and androsterone (A); artificial synthetic estrogens or androgens such as  $17\alpha$ -ethynodiol (EE2), Norgestrel (N), and Trenbolone (Tr); phytoestrogens including isoflavonoids and coumestrol as well as other industrial compounds such as bisphenol A, nonylphenol etc. These chemicals are found in the aquatic environment. Moreover, the wastewater plants are known to be the major source of these EDCs. Natural and synthetic EDCs are released into the environment by humans, animals and industry; mainly through the sewage treatment plants before reaching the receiving bodies (soil, surface water, sediment and ground water), EDCs' main distribution in the environment is shown in Figure 12 [75]. EDCs are one of major concern towards the environmentalist and it has to be dealt adequately/properly. The possible option is the complete removal of EDCs from the environment. Since, sewage plants are the major source of EDCs, hence, it has to be removed completely from the sewage at sewage plants prior to final release to the environment. Moreover, several methodologies are adopted for its removal/degradation using the physical and chemical methods however, in the last couple of decades the chemical treatment based on the ferrate(VI) technology received an enhanced attention because of the reasons underlying:

- (i) relatively higher oxidation potential of Fe(VI), (ii) the non-toxic by-products generated in the degradation process, and (iii) fast and effective treatment.

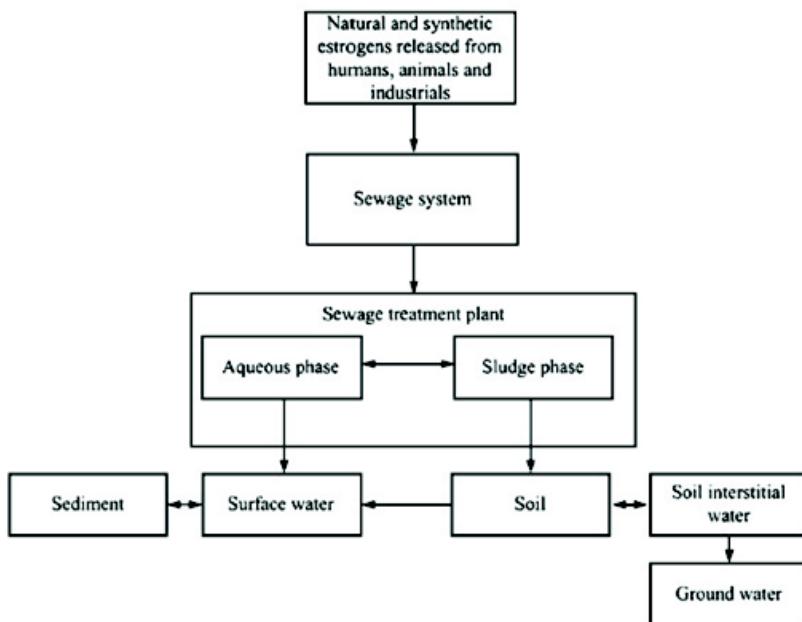


Fig. 12. EDCs distribution in the environment [75].

The reactivity of commonly used oxidants as mentioned previously (Table 3) is  $\text{FeO}_4^{2-} > \text{O}_3 > \text{S}_2\text{O}_4^{2-} > \text{H}_2\text{O}_2 > \text{Cl}_2 > \text{ClO}_2$ . Keeping in view the several studies showed the effectiveness of ferrate(VI) for such studies. The degradation of estrone (E1), 17 $\beta$ -estradiol (E2) and 17 $\alpha$ -ethynylestradiol (EE2) was conducted with varied ferrate(VI) doses and solution pH. It was demonstrated that at pH 9.0 the maximum degradation of these compounds took place and complete degradation was reported for *Ca* three times of Fe(VI) dose (*cf* Figure 13) [76]. Similarly, ferrate(VI) was found to be superior oxidant than usual electrochemical reduction of bisphenol-A, E2 and 4-tert-octylphenol (*cf* Figure 14) [77].

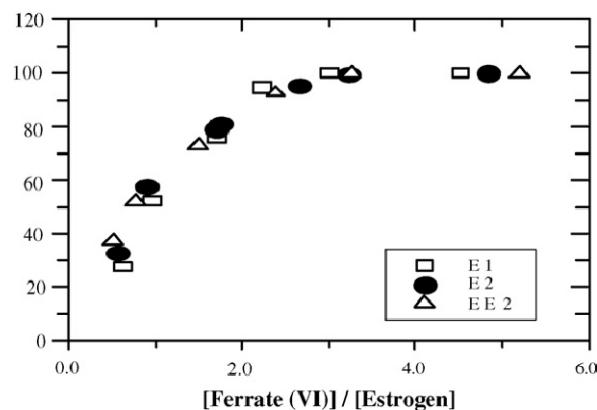


Fig. 13. Degradation of estrogens at pH 9, ferrate dose vs. removal percentage [76].

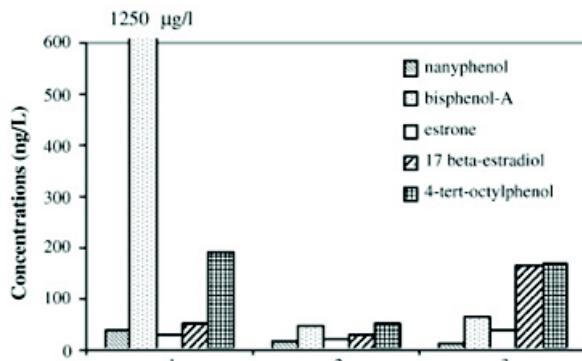


Fig. 14. Comparative EDCs residual concentrations. (1) Wastewater sample taken from the post-sedimentation; (2) treated sample with ferrate oxidation; (3) treated sample with electrochemical oxidation [77].

The kinetic model and path of degradation process for five different EDCs viz., BPA (Bisphenol A), EE2 ( $17\alpha$ -ethynylestradiol), E1 (Estrone), E2 ( $\beta$ -estradiol) and E3 (Estriol) are studied using the LC/MS and GC/MS spectroscopic methods [78]. The proposed model is useful to discuss here. The dissociated ( $EDC^-$ ) and un-dissociated ( $EDC'$ ) form of EDCs were considered using the known  $pK_a$  values along with the species of ferrate (VI) i.e.,  $FeO_4^{2-}$  and  $HFeO_4^-$  in the studied pH region using the  $pK_a^3$  for ferrate(VI). The oxidation reactions may be summarized as:

$$\left( \frac{d[EDC]}{dt} \right)_1 = -[FeO_4^{2-}] (k_1[EDC'] + k'_1[EDC^-]), \quad (35)$$

$$\left( \frac{d[EDC]}{dt} \right)_2 = -[HFeO_4^-] (k_2[EDC'] + k'_2[EDC^-]). \quad (36)$$

The overall rate of EDC compound degradation was assumed to be sum of these two rates and can be expressed as:

$$\frac{d[EDC]}{dt} = \left( \frac{d[EDC]}{dt} \right)_1 + \left( \frac{d[EDC]}{dt} \right)_2. \quad (37)$$

The corresponding rates of oxidant ( $FeO_4^{2-}$  and  $HFeO_4^-$ ) reduction during the reaction were expressed by equation (38) and (39), respectively:

$$\frac{d[FeO_4^{2-}]}{dt} = -[FeO_4^{2-}] (k_{11}[EDC'] + k'_{11}[EDC^-]), \quad (38)$$

$$\frac{d[HFeO_4^-]}{dt} = -[HFeO_4^-] (k_{21}[EDC'] + k'_{21}[EDC^-]). \quad (39)$$

In the case of the ferrate(VI) reduction, the overall rate of ferrate(VI) reduction was assumed to be the sum of the two rates, plus the thermodynamic decomposition of ferrate in water; this can be expressed as:

$$\frac{d[Fe(VI)]}{dt} = \frac{d[FeO_4^{2-}]}{dt} + \frac{d[HFeO_4^-]}{dt} - k_d[Fe(VI)], \quad (40)$$

where  $k_d$  is the decomposition constant of ferrate(VI) in the solution. Since, at higher pH range (i.e., 8~10), the self decomposition of ferrate(VI) is almost negligible hence, may be ignored. Therefore, the rate expression may be simplified to:

$$\frac{d[Fe(VI)]}{dt} = \frac{d[FeO_4^{2-}]}{dt} + \frac{d[HFeO_4^-]}{dt} \quad (41)$$

According to the equilibrium of the two ferrate species at different pH, the concentrations of  $HFeO_4^-$  and  $FeO_4^{2-}$  should have specific ratio at a given pH. The species concentration may be given as:

$$[HFeO_4^-] = \alpha_{HFeO_4^-} [Fe(VI)] = \frac{[HFeO_4^-]}{[Fe(VI)]} [Fe(VI)], \quad (42)$$

$$[FeO_4^{2-}] = \alpha_{FeO_4^{2-}} [Fe(VI)] = \frac{[FeO_4^{2-}]}{[Fe(VI)]} [Fe(VI)], \quad (43)$$

Moreover, the relationship between the concentrations of un-dissociated and dissociated EDCs and pH can be described by the following expressions:

$$[EDC^-] = \frac{k_{aEDC}}{[H^+] + k_{aEDC}} [EDC], \quad (44)$$

$$[EDC'] = \frac{H^+}{[H^+] + k_{aEDC}} [EDC], \quad (45)$$

$$\frac{d[EDC]}{dt} = - \left( k_1 \alpha_{FeO_4^{2-}} \frac{H^+}{[H^+] + k_{aEDC}} + k'_1 \alpha_{FeO_4^{2-}} \frac{k_{aEDC}}{[H^+] + k_{aEDC}} + k_2 \alpha_{HFeO_4^-} \frac{H^+}{[H^+] + k_{aEDC}} + k'_2 \alpha_{HFeO_4^-} \frac{k_{aEDC}}{[H^+] + k_{aEDC}} \right) \times [Fe(VI)] = k_e [EDC] [Fe(VI)], \quad (46)$$

$$\frac{d[Fe(VI)]}{dt} = - \left( k_{11} \alpha_{FeO_4^{2-}} \frac{H^+}{[H^+] + k_{aEDC}} + k'_{11} \alpha_{FeO_4^{2-}} \frac{k_{aEDC}}{[H^+] + k_{aEDC}} + k_{21} \alpha_{HFeO_4^-} \frac{H^+}{[H^+] + k_{aEDC}} + k'_{21} \alpha_{HFeO_4^-} \frac{k_{aEDC}}{[H^+] + k_{aEDC}} \right) \times [EDC] [Fe(VI)] = k_f [EDC] [Fe(VI)]. \quad (47)$$

Dividing equation (46) by (47) and integrating  $d[EDC] = (k_e/k_f) d[Fe(VI)]$  with the initial conditions (when  $t=0$ ,  $[EDC]=[EDC]_0$  and  $[Fe(VI)] = [Fe(VI)]_0$ , a pair of second-order equations for EDC degradation and Fe(VI) reduction versus reaction time were expressed by the following equations (48) and (49), respectively:

$$[EDC] = \frac{k_e [EDC]_0 [Fe(VI)]_0 - k_f [EDC]_0^2}{k_e [Fe(VI)]_0 e^{(k_e [Fe(VI)]_0 - k_f [EDC]_0)t} - k_f [EDC]_0}, \quad (48)$$

$$[Fe(VI)] = \frac{k_f [EDC]_0 [Fe(VI)]_0 - k_e [Fe(VI)]_0^2}{k_f [EDC]_0 e^{(k_f [EDC]_0 - k_e [Fe(VI)]_0)t} - k_e [Fe(VI)]_0}, \quad (49)$$

where

$$k_e = \frac{k_1 k_{aFE} [H^+] + k'_1 k_{aFE} k_{aEDC} + k_2 [H^+]^2 + k'_2 [H^+] k_{aEDC}}{[H^+]^2 + [H^+] k_{aEDC} + [H^+] k_{aFE} + k_{aFE} k_{aEDC}}$$

$$k_f = \frac{k_{11} k_{aFE} [H^+] + k'_{11} k_{aFE} k_{aEDC} + k_{21} [H^+]^2 + k'_{21} [H^+] k_{aEDC}}{[H^+]^2 + [H^+] k_{aEDC} + [H^+] k_{aFE} + k_{aFE} k_{aEDC}}$$

The rate constants  $k_1$ ,  $k_1'$ ,  $k_2$ ,  $k_2'$ ,  $k_{11}$ ,  $k_{11}'$ ,  $k_{21}$  and  $k_{21}'$  were obtained by the least-square fitting method. Results obtained were given in Table 7. Similarly, the fitted results and experimentally observed data at pH 9.2 with  $[EE2]_0 = [E1]_0 = [E2]_0 = [E3]_0 = 0.01 \text{ mM}$ ,  $[EPA]_0 = 0.1 \text{ mM}$  and  $[Fe(VI)]_0 = 0.05 \text{ or } 0.1 \text{ mM}$  were shown in Figure 15. These results, again suggested that protonated species of ferrate(VI) i.e.,  $HFeO_4^-$  is more reactive than non-protonated species  $FeO_4^{2-}$  towards all these EDCs studied. However, the dissociated (ionized) EDCs are more reactive towards the protonated ferrate(VI).

Compound	$k_1 (\text{M}^{-1}\text{s}^{-1})^a$	$k_1' (\text{M}^{-1}\text{s}^{-1})^b$	$k_2 (\text{M}^{-1}\text{s}^{-1})^c$	$k_2' (\text{M}^{-1}\text{s}^{-1})^d$
BPA	$2.80 \times 10^2$	$5.16 \times 10^2$	$8.20 \times 10^2$	$7.76 \times 10^4$
EE2	$3.05 \times 10^2$	$8.52 \times 10^2$	$9.10 \times 10^2$	$5.11 \times 10^5$
E1	$7.10 \times 10^2$	$8.97 \times 10^2$	$9.80 \times 10^2$	$5.31 \times 10^5$
E2	$7.32 \times 10^2$	$9.41 \times 10^2$	$1.08 \times 10^3$	$5.40 \times 10^5$
E3	$9.28 \times 10^2$	$1.003 \times 10^3$	$1.12 \times 10^3$	$5.44 \times 10^5$

<sup>a</sup>  $FeO_4^{2-}$ ; undissociated EDC; <sup>b</sup>  $FeO_4^{2-}$  dissociated EDC; <sup>c</sup>  $HFeO_4^-$  un-dissociated EDC; <sup>d</sup>  $HFeO_4^-$  dissociated EDC

Table 7. Rate constants of EDC degradation with Ferrate(VI) [reproduced from [78]]

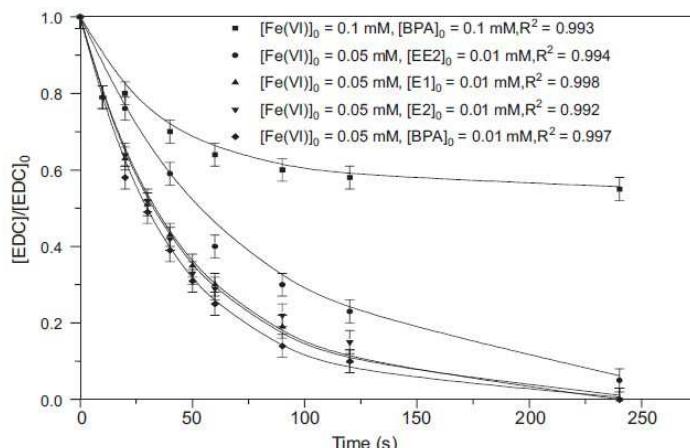


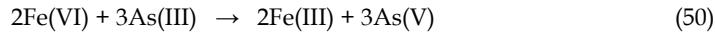
Fig. 15. Composition between experimental data and kinetic model for the degradation of EDCs by ferrate(VI) [78].

### 3. Fe(VI) in the removal of non-degradable pollutants

The non-degradable impurities particularly the heavy metal toxic ions or radionuclides is received a greater importance in the treatment of waste waters. These metallic impurities are present in the aquatic environment either in its free form or to its complexed form. Ferrate(VI) as discussed (reaction (14)) reduced to Fe(III), which possessed with fairly good coagulation/flocculation properties hence, able to coagulate these impurities and with sedimentation/filtration can be removed. Moreover, the Fe(III) as iron(III) hydroxides are known to be a potential adsorbent, possibly can remove the free metallic impurities even by adsorption process.

### 3.1 Removal of metal cations/anions

The arsenic (III) oxidation to As(V) and hence, the removal of As(V) by reduced Fe(III) via coagulation process was effectively achieved [65]. The two moles of Fe(VI) required to oxidize three moles of As(III) (reaction 50). The oxidation of As(III) followed second order rate law at pH 8.4 to 9.0. It was noted that the complete oxidation took place within a second.



Further, it was demonstrated that with even smaller dose of Fe(VI) along with the supplementary dose of Fe(III) may achieve the efficiency to remove the arsenic from the arsenic contaminated river water (Nakdong River, Korea).

Potassium ferrate(VI) is an potential chemical to remove several metal cations/anions including  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Hg}^{2+}$  from aqueous solutions via oxidation/coagulation/adsorption process using lower dose of Fe(VI) 10-100 mg/L [79].

Similarly, the metal complexed species were studied and discussed previously particularly the metal(II) cyanide complexes [58,63,66-67]. An interesting study using Cu(II)and Ni(II) cyanide complexed were used and showed that complete degradation of cyanide along with the complete removal of free copper and partial removal of nickel (*cf* Figure16) [80]. Further the study was extended to employ it for the treatment of real electroplating wastes containing the copper and nickel complexed cyanides [34]. Recently, the removal of As(III) by Fe(VI), ferrate(VI)/Fe(III) and ferrate(VI)/Al(III) salts was studied as a function of pH (8.0 to 6.0) and anion concentration [81]. Removal of As(III) was increased with decrease in pH from 8 to 6. The effects of different anions on the removal of As(III) in the ferrate(VI)/Al(III) system at pH 6.5 (*cf* Figure 17). It was suggested that phosphate and silicate formed inner-sphere complexes and compete strongly with arsenic for Fe or Al oxy/hydroxide surfaces and such competition exist only at higher concentrations of phosphate and silicate, causing an apparent decrease in removal efficiency of the system. Bicarbonate also influenced the removal of As(III), but much higher levels were needed than that of phosphate and silicate [81]

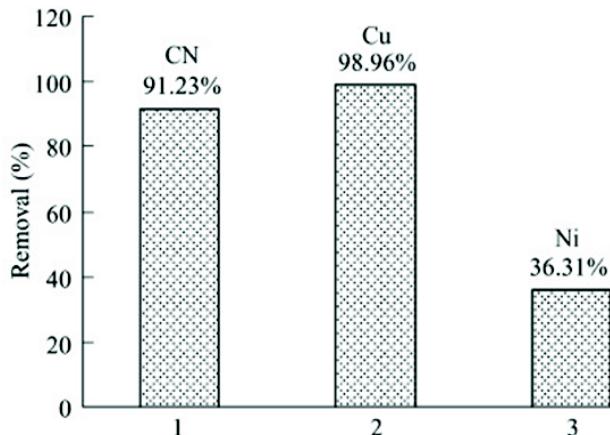


Fig. 16. Fe(VI) treatment for CN oxidation and simultaneous removal of Cu and Ni in CN-Cu-Ni system. CN: 1.00 mmol/L, Cu: 0.100 mmol/L, Ni: 0.170 mmol/L, Fe(VI) dose: 2 mmol/L [80].

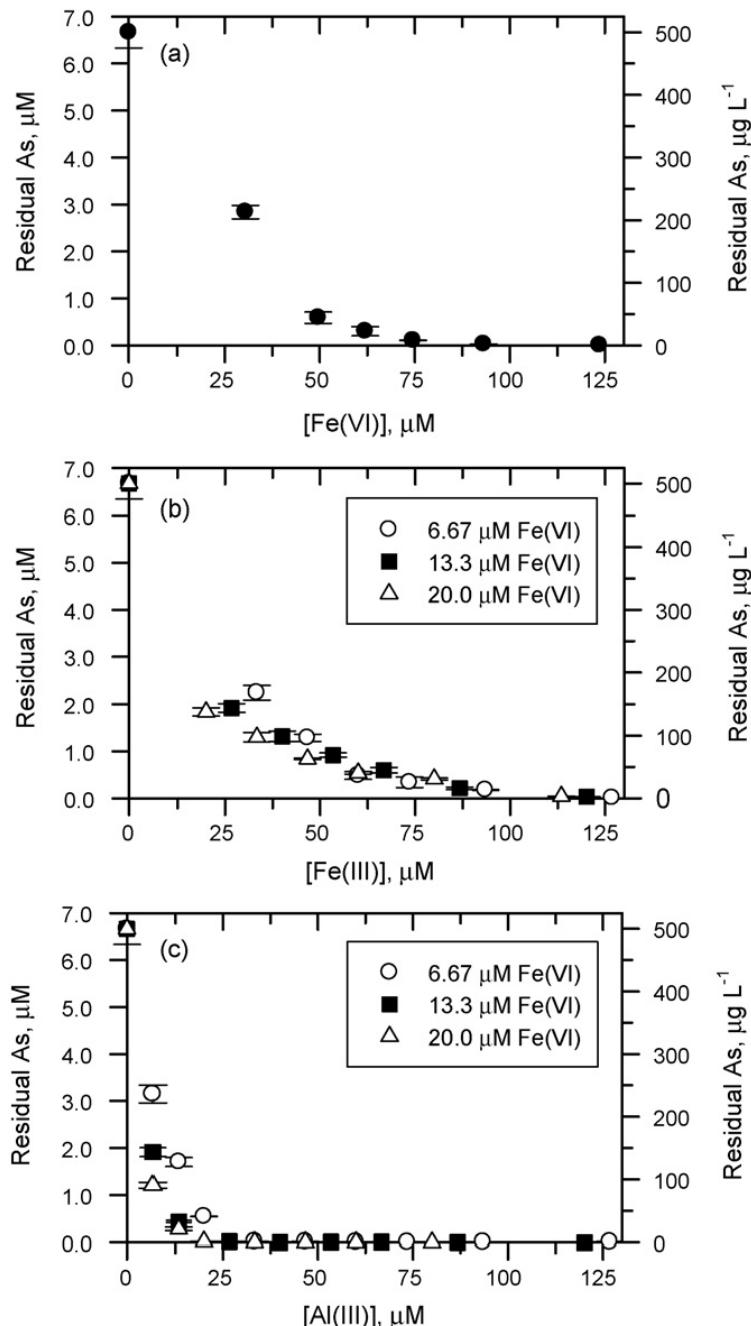


Fig. 17. Removal of arsenite by Fe(VI) (a), Fe(VI)/Fe(III) salts (b), and Fe(VI)/Al(III) salts (c) at pH 6.5. Initial concentration = 500 µg As(III)/L [81].

The decomplexation of Zn(II)-NTA with Fe(VI) showed second order rate kinetics and the rate constant value was found to be  $8.80 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}$ . Further, the reaction was almost unaffected in presence of 1000 times NaNO<sub>3</sub>, NaCl and NaClO<sub>4</sub>. However, it was greatly suppressed in presence of Na<sub>2</sub>SO<sub>3</sub> and NaNO<sub>2</sub> electrolyte. This suggests that Fe(VI) prefer the oxidation of SO<sub>3</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup> rather the Zn(II)-NTA complex [82].

Interestingly, the americium and plutonium radionuclides were treated with ferrate(VI) at pH 11.5-12.0 and results showed that the treated water samples contain significantly less radioactivity [83]. This was assumed that these radionuclides are coagulated with reduced Fe(III). Similarly, other radionuclides are treated with Fe(VI) showed, Fe(VI) could play a wider possible role in radioactive waste management studies [84-85].

#### 4. Other possible applications of Fe(VI) in the remediation of wastewater treatment

The possible role of Fe(VI) is in the treatment of real wastewaters and to study the parameters involved. The various physical/chemical parameters studied and showed the applicability of Fe(VI) in the remediation of the waste water treatment. In addition the important aspect of ferrate(VI) technology is the property of disinfection. In the proceeding section the disinfection of Fe(VI) is discussed and possible mechanistic aspects are discussed in detail.

##### 4.1 Disinfection of wastewater

Coagulation and oxidation/disinfection are to be the important unit processes associated with the water or wastewater treatment. The role of ferrate(VI) towards the degradation of several degradable materials shown to be promising and it possessed remarkably good coagulating/adsorbing capacity via the reduced Fe(VI) into Fe(III). The disinfection was rather, studied scarcely but several reports encourages the potential use of ferrate(VI) towards the disinfection reagent to be applied in the wastewater treatment plants.

The disinfection property of ferrate(VI) was first optimized to kill two pure laboratory cultures of bacteria (Non-recombinant *Pseudomonas* and Recombinant *Pseudomonas* [39]). At a dose of 0-50 ppm as FeO<sub>4</sub><sup>2-</sup>, the bacteria were removed completely. The oxidation of *E. Coli* DNA polymerase-I by Fe(VI) resulted in loss of polymerization and 3-5 exonuclease activity and thus the irreversible inactivation of the enzyme was reported [86]. Moreover, the reactivity of deoxyribonucleosides by Fe(VI) caused DNA chain cleavage through a mechanism in which base loss is followed by β-elimination at the abasic site [87]. The results suggested irreversible inactivation of *E. Coli* by ferrate(VI).

The ferrate(VI) showed sufficient disinfection capability as to kill the *Escherichia coli* (*E. coli*). At pH 8.2 with a dose of 6 mg/L as Fe, the *E. coli* percentage kill was 99.9% but when the contact time was extended to 18 min even with the reduced dose of 2.4 mg/L as Fe facilitate the complete kill of *E. coli* [88]. The results also demonstrated that the disinfecting ability of FeO<sub>4</sub><sup>2-</sup> increased markedly if water pH was below 8.0. Similarly, the secondary effluent disinfection study showed 99.9% of total *coliforms* and 97% of the total viable bacteria were removed at a dose of 8 mg/L of ferrate(VI) (cf Figure 18) [89].

The real sewage wastewater and a model water *E. coli* (concentration  $3.2 \times 10^8 / 100\text{mL}$ ) were used to assess the Fe(VI) capability as coagulant behavior (compared to ferric and aluminum

sulfate) for real wastewater and disinfection for the model *E.coli* water (compared with sodium hypochlorite) [90]. The Fe(VI) showed significantly better performance over ferric and aluminum sulphate. Moreover, the disinfection towards *E. coli* was also comparatively better than hypochlorite. In a line the comparative performance of ferrate(VI) with ferric sulfate and aluminum sulfate are carried and reported that ferrate possessed better treatment chemical (cf Table 8) [91].

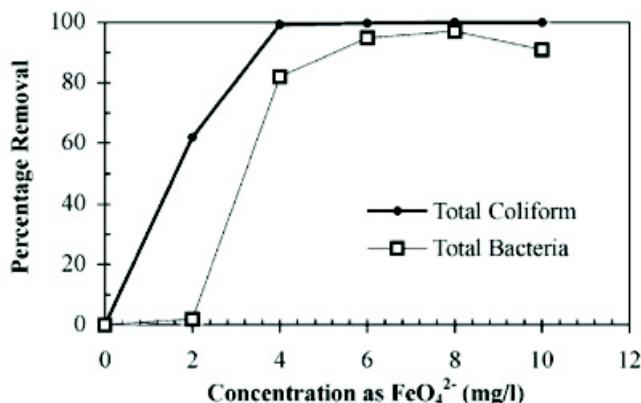


Fig. 18. Total *coliform* organisms and total bacteria removal with Fe(VI) [89].

	AS	FS	Fe(VI)
pH	6.75-7.48	6.75-7.48	7
Optimum dose as Al(III)) or Fe(III) (mmol/L)	0.37	0.36	0.36
Turbidity removal (%)	80	86	94
Colour (Vis400-abs) removal (%)	50	50	92
Total COD removal (%)	6	16	32
Dissolved COD removal (%)	4	7	14
Bacteria inactivation (in $\log_{10}$ terms) <sup>a</sup>	1	1.05	>4

<sup>a</sup> AS and FS achieved 1- $\log_{10}$  bacteria inactivation at doses >0.50 mmol/L as either Al or Fe, whilst FR achieved >4- $\log_{10}$  bacteria inactivation at doses <0.27 mmol/L as Fe.

Table 8. Comparative performance of coagulants at optimum dose [91]

The disinfection kinetic model was proposed by Chick-Watson relation (equation (51)) as to derive the rate constants:

$$\frac{N}{N_0} = e^{-kt} \quad (51)$$

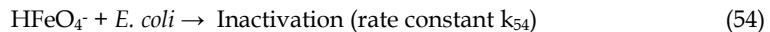
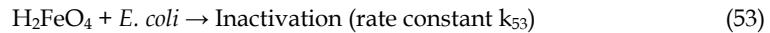
Where, N and  $N_0$  are the number concentrations of the organisms remaining and originally, respectively, t is disinfectant-organism contact time, and k is the rate constant ( $\text{time}^{-1}$ ); and k

can be written as  $k = k' C^b$  to relate the rate constant of inactivation to the disinfectant concentration  $C$ .  $b$  is termed as dilution coefficient and can be obtained by the slope of a log-log plot of  $t$  vs  $C$ . Previously, the  $k$  was evaluated for *E. coli* using the equation (51) at different pH for the disinfection of *E. coli* [90].

The modified Delayed Chick-Watson law with time averaged Fe(VI) concentration (equation (52)) was used in order to discuss the kinetics of the inactivation [27,92].

$$\log(N|N_0) = -k[\overline{Fe(VI)}]T = -k\bar{C}T \quad (52)$$

where  $N_0$  is the initial number of viable *E. coli* (CFU mL<sup>-1</sup>),  $N$  is the remaining number of viable *E. coli* (CFU mL<sup>-1</sup>) at time  $T$  (min),  $\overline{[Fe(VI)]} = \int_0^T [Fe(VI)]dt/T$  is the time averaged Fe(VI) concentration, which can be determined by integrating time-dependent Fe(VI) concentration profiles with time. This can be predicted by using self-decomposition rate constants of Fe(VI) or measured directly. This model is based on the assumption that the degree of *E. coli* inactivation ( $\log(N/N_0)$ ) is proportional to the time-dependent amount of *E. coli* exposed to ( $\overline{[Fe(VI)]}T$ ), which reflects a more realistic oxidative environment for *E. coli* inactivation. It was further, demonstrated the inactivation ability of different Fe(VI) species using the different  $pK_a$  values of ferrate(VI) [92]. The different species of Fe(VI) would have variable reactivity towards the inactivation of *E. coli* hence would have different rate constants of inactivation:



By assuming an additive inactivating efficiency for  $H_2FeO_4$ ,  $HFeO_4^-$  and  $FeO_4^{2-}$  toward *E. coli*, the log inactivation level of *E. coli* can be expressed in the form of equation (56):

$$\begin{aligned} \log\left(\frac{N}{N_0}\right) &= -\{k_{53}\overline{[H_2FeO_4]} + k_{54}\overline{[HFeO_4^-]} + k_{55}\overline{[FeO_4^{2-}]}\}T \\ &= -\int_0^T k_{53}\overline{[H_2FeO_4]} + k_{54}\overline{[HFeO_4^-]} + k_{55}\overline{[FeO_4^{2-}]}dt. \end{aligned} \quad (56)$$

Accordingly, the  $k_{obs}$  can be expressed as equations (54), which can be deduced from the comparison of equation (56) with equation (52):

$$k_{obs} = \alpha_0 k_{53} + \alpha_1 k_{54} + \alpha_2 k_{55} \quad (57)$$

$$\alpha_0 = \frac{[H_2FeO_4]}{[Fe(VI)_T]} = \frac{[H^+]^2}{T}, \quad (58)$$

$$\alpha_1 = \frac{[HFeO_4^-]}{[Fe(VI)_T]} = \frac{k_a^3[H^+]}{T}, \quad (59)$$

$$\alpha_2 = \frac{[FeO_4^{2-}]}{[Fe(VI)_T]} = \frac{k_a^3 k_a^4}{T}, \quad (60)$$

$$\text{where } T = [\text{H}^+]^2 + k_a^3 [\text{H}^+] + k_a^3 k_a^4$$

Hence, the three inactivation constants ( $k_{53}$ ,  $k_{54}$  and  $k_{55}$ ) can be estimated with measured pH dependence data. The data obtained with this study showed that  $\text{HFeO}_4^-$  and  $\text{H}_2\text{FeO}_4$  were found to be 3 and 265 times as effective as  $\text{FeO}_4^{2-}$  at least towards the inactivation of *E. coli* [92].

Moreover, it was reported that ferrate(VI) can rapidly inactivate the *f2 Coliphage* at low concentrations; 99% of *f2 Coliphage* was inactivated at 1 mg/L of ferrate(VI) in 5.7 min at pH 6.9 and only 0.77 min at pH 5.9. A higher dose (10 mg/L of ferrate(VI)) was required in order to achieve 99.9% inactivation at pH 7.8 with a contact time to 30 min [93,94].

#### 4.2 Degradation of pharmaceuticals present in aquatic environment

The enhanced level of pharmaceuticals present in the aquatic environment shown a greater concern for its degradation/removal from the aquatic environment. These chemicals includes with variety of antibiotics. Several reports demonstrated the use of advanced oxidation using  $\text{O}_3/\text{H}_2\text{O}_2$ , UV/ $\text{H}_2\text{O}_2$ , Fenton/Photon-Fenton or UV/ $\text{TiO}_2$  processes or even simple biological or chemical degradation employed to degrade these micro pollutants from the wastewater. However, the use of ferrate(VI) attained greater interest in recent past because of green treatment and significant reactivity of the compound (vide Table 3). Several sulphur containing antibiotics including sulfamethoxazole, sulfametazine, sulfamethizole, sulfadimethoxine, sulfasoxazole etc. were treated with ferrate(VI) and rate expressions were obtained. It was reported that 1:1 stoichiometry occurred in the degradation of these drugs with Fe(VI) and rate law for each reactant is of pseudo first-order using excess of Fe(VI). Further, second order rate constants were evaluated and given in Table 9 [95-97].

Sulfonamide	$k_{\text{HFeO}_4}$ ( $10^3 \text{ M}^{-1}\text{s}^{-1}$ )		$k_{\text{FeO}_4}$ ( $10^1 \text{ M}^{-1}\text{s}^{-1}$ ) SH	$K_{\text{app}}$ ( $10^3 \text{ M}^{-1}\text{s}^{-1}$ ) pH 7.0	$t_{1/2}$ (s)
	SH	S·			
Sulfamethoxazole	30.0	0.17	0.12	1.50	91
Sulfametazine	1.90	0.55	22.5	0.87	157
Sulfamethizole	22.3	0.22	-	0.64	214
Sulfadimethoxine	18.8	0.38	-	-	-
Sulfasoxazole	11.0	2.42	-	0.85	161

Half lives for the dose of 1 mg/L of  $\text{K}_2\text{FeO}_4$  at pH 7.0 and 25 °C

Table 9. Second-order rate constants for reactions of sulfonamides at 25 °C [95]

#### 5. Conclusions

The ferrate(VI) which possessed significantly high oxidation capability along with significantly high coagulation/flocculation and disinfection properties showed that it may be one of potential chemical towards the several aquatic environmental remediation strategies. Moreover, as the ferrate(VI) treatment is absolutely free from the occurrence of

toxic/harmful by-products hence, found to be more environmentally benign or termed as 'Green Chemical' and the ferrate(VI) technology may be known as "Green Technology".

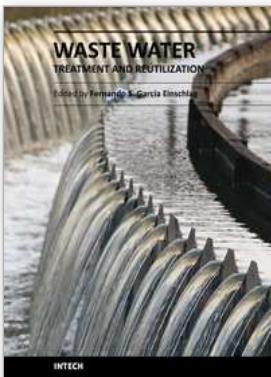
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