

APPLICATIONS OF FERRATE(VI) IN THE TREATMENT OF WASTEWATERS

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Abstract : The novel behavior of ferrate(VI) has received an increased attention for its possible applications in various purposes particularly in the treatment of waste/effluent waters. It possess relatively high oxidizing capacity and the reduced ferrate(VI) into Fe(III) 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 a 'green chemical' and further enhances its widespread uses in various purposes. Here an attempt has been made to review the applications of ferrate(VI) in the treatment of waste waters and also its possible future applications in the wastewater treatment technology.

Key Words : Ferrate(VI), wastewater treatment, oxidant, coagulant

INTRODUCTION

The increased level of industrialization and urbanization poses serious threat among the nations to handle properly the waste and wastewaters and also to propose easily viable waste management program to deal with the problem. The fresh water resources of the world are under tremendous stress as fresh water is greatly contaminated by the industrial and domestic effluents as well as toxins found in nature such as arsenic, the existing water treatment technologies are not found enough to meet the problem. Hence, there is a demand to investigate and develop more and more viable and cost effective wastewater treatment technologies for more effective and efficient methods in the sustainable fresh water supply. In this regard, the environmental regulation concerning to the public health requires that the wastewater

collected from municipalities and communities must be treated below the given standards before it return to surface waters or to the land or reuse. An advanced primary treatment aiming to enhance the removal of colloidal particles and organic constituents from wastewaters is a basic step and a starting point, leading to fewer remaining particles and organic pollutants, which is favorable to the subsequent biological and physico-chemical treatment processes. The important part of the treatment comprises two steps *viz.*, first the oxidation/disinfectant of the wastewater followed by the coagulation of the waste materials.¹⁾ Disinfectant is designed to kill the harmful organisms (e.g., bacteria and viruses) and oxidation is used to degrade various organic/inorganic contaminants. Further, the coagulant destabilizes colloidal impurities and transfers small particles into large aggregates and adsorbs dissolved organic materials onto the aggregates, which can then be removed by sedimentation and filtration.

Similarly, during the process of treatment of

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municipal and/or industrial wastewaters, large amount of sludge is to be obtained which contains various types of organic and inorganic compounds.²⁻⁴⁾ The dewatered sludge (often called as biosolids), which has obtained after proper and adequate treatment can have various useful economic values as in the soil conditioner and in fertilizers too. However, the untreated and/or partially treated samples pose a serious threat to human health and ecosystem. Therefore, sludge management is becoming a major issue of the 21st century.⁵⁾ Moreover, a number of organic sulphides and amines produced during wastewater treatment contribute on-site odors, which would become a severe problem for human life.⁶⁾ Hence, always there is an increasing demand of innovative sludge management practice, which can effectively treat a wide range of odor producing contaminants and health hazardous pathogenic organisms.²⁾

The presence of several pharmaceuticals in the aquatic environment may causes for several eco-toxicological effects.^{7,8)} Literature showed several treatments is to be applied for the pharmaceuticals treatment in drinking water.⁹⁻¹³⁾ Recently, ozonation and filtration with granular activated carbon were shown promising to remove pharmaceuticals.¹⁰⁾ Similarly, other advanced oxidation processes (AOP)¹³⁾ and photocatalytic oxidation¹²⁾ have also been reported for removal of pharmaceuticals from the aquatic systems. Recently, kinetics of the oxidation of pharmaceuticals with ozone and hydroxyl radicals ($\cdot\text{OH}$) has been studied extensively in order to predict removal of pharmaceuticals.¹¹⁾ Looking into the oxidation of pharmaceuticals there is an increasing demand for the newer type of materials, which are found to be efficient and also have environmentally friendly by products. In a line, the unusual disposal of surfactant in our aquatic environment also causes for deleterious quality of freshwater¹⁴⁾ as it restricts both settling of floating particles and dissolution of atmospheric oxygen into natural waters. Surfactants are surface active reagents having several organic compounds both the types

i.e., hydrophobic (e.g., alkyl chain) and hydrophilic groups (e.g., ammonium salts) and the sources of these materials are detergent, personal care products or indirectly in production and processing of such materials. The biodegradation of cationic surfactant is likely to be cumbersome as to existing waste treatment process however, the anionic type surfactants can be degraded easily as reported earlier.^{15,16)} Moreover, the process of degradation is too slow hence, it further requires a newer type of material which, can effectively and efficiently degrade the anionic as well as cationic type of surfactants.¹⁴⁻¹⁸⁾

The contamination of underground water with arsenic in Bangladesh and nearby regions is becoming a serious concern as due to increased number of cancer patient in that region with chronic arsenic poisoning.¹⁹⁾ As(III) is comparatively more toxic and mobile than As(V) hence, it is required to oxidize the As(III) into As(V) and followed by the coagulation step to remove completely the arsenic from the water bodies.²⁰⁾ Hence, for the oxidation or coagulation of arsenic some material is needed which can show efficient behavior also are found to be eco-friendly.

Hence, literature survey reveals that there is an increasing demand to innovate and modify the technologies for waste water treatment by using some alternative chemicals which has a greater efficiency, selectivity and also possess the more environmentally friendly.

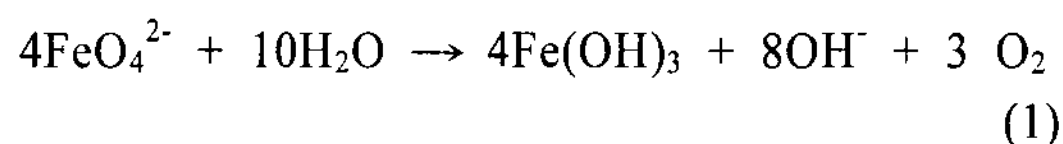
In this connection, the various facets of "ferrate" were well investigated. Owing to its multifunctional properties, it is likely to be a good plausible alternative to replace the existing technology. Moreover, the non-toxic and eco-friendly by-products further exaggerate its application in such studies. Although couple of reviews already published in the ferrate chemistry and their multifunctional behavior^{21,22)} still it always worth finding to review the literature on ferrate particularly its possible applications in wastewater treatment as dealing with the recent topics related to the oxidizing/

disinfectant properties of the ferrate such as the treatment of biosolids, wastes containing pharmaceuticals and also the treatment of arsenic contamination. Hence, here an attempt has been made to review critically the various uses and possible applications of ferrate(VI) in wastewater treatment along with their preparation processes.

FERRATE(VI): A GREEN CHEMICAL

The term 'ferrate' usually referred for the higher valence states of Fe(III), it may include +4, +5, and +6 states. Among all these states Fe(VI) seems to be the best known and well studied as due to its stability and occurrence.^{23,24)} The uses and applications of ferrate are wide ranged as due to its high oxidizing capacity since the redox potential of ferrate(VI) is much higher than the redox potentials of common oxidizing agents usually used for various purposes. In aqueous solutions, the ferrate ion (FeO_4^{2-}) is reduced and generates both ferric hydroxide precipitate and nascent oxygen (Equation 1). Hence, it has an enhanced attention to be applied in water treatment process as it can easily oxidize even stable organic and mineral materials; bactericide agents etc. Also the ferric hydroxide reduced from ferrate has the property of flocculating and coagulating. Therefore, the ferrate can replace the chlorine in the pre-oxidation stage of water and partially the iron and aluminum salts (FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$), which are commonly used as coagulant and flocculating agents. In addition, from the decomposition of the ferrate(VI) (Equation 1), it results a basic medium favorable for the precipitation/adsorption of heavy metals as hydroxides. Moreover, the by-products generated during the complete process are non-toxic and do not have any adverse effects towards the environment or human health. Hence, the ferrates are termed, as 'green chemical' and interestingly the single chemical possess several properties, which ultimately prompted to explore further the chemistry of ferrates and also their

possible applications in various areas of interest.



FERRATE PREPARATION

Although the ferrate(VI) was known and synthesized centuries back as by Stahl²⁵⁾ and Poggendorf²⁶⁾ also described by Mellor²⁷⁾ in the year 1702 but due to its stability and cumbersome preparation process and low yield, a scanty of work was done during the period. However, in the 20th century much attention was given for the preparation of stable ferrate(VI) salts with the increased yield. This may be due to its unique behavior and enhanced applications in various areas. Literature survey reveals that ferrate(VI) can be produced by dry and wet methods.^{23,28,29)} Dry synthetic methods are usually performed using a thermal technique whereas wet methods include chemical and electrochemical techniques. Briefly we summarize all these methods for preparation of ferrate(VI).

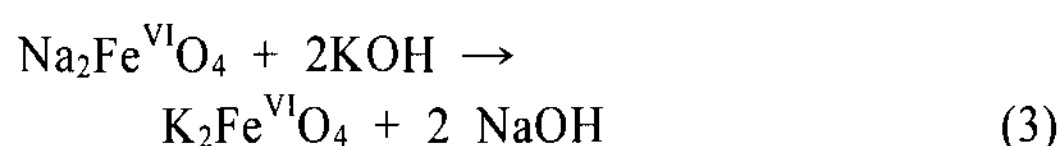
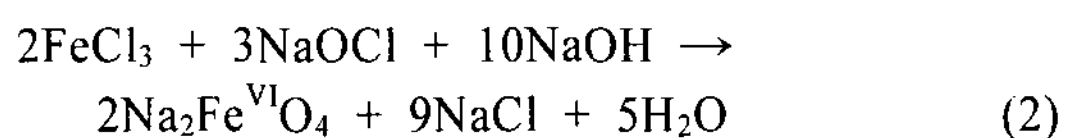
Electrochemical Method

Ferrate was first prepared electrochemically in 1941²⁶⁾ by anodic oxidation of iron electrode in strongly alkaline solution. Later, Electrochemical ferrate(VI) synthesis was done by Tousek during his Ph.D. work.³⁰⁻³²⁾ It was reported that 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 is greatly reduced in this environment.³³⁾ It was found by Pick³⁴⁾ that the current yield during electrochemical production increased with the carbon content in the iron anode material used; the current yields were 15% for raw iron, 27% for steel and 50% for cast iron at a current density of 10 A m^{-2} and a NaOH concentration of 16.5M. The carbon content (0.08-0.90%) again in iron, which was

used as anode in ferrate preparation electrochemically, was studied very systematically and it was observed that the higher the carbon content higher the current efficiency.^{35,36)} More or less similar findings were obtained by using the pure iron containing 99.95% Fe and less than 0.005 wt % C, the white cast iron containing 3.16 wt % C in the form of iron carbide (Fe₃C) and the grey cast iron with 3.43 wt % of carbon, mainly in the form of graphite (76.7% of C).³⁷⁻⁴²⁾ Bouzek recently 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.⁴³⁾ White cast iron was found to be the most suitable anode materials in terms of ferrate current yield. The NaOH-KOH system having low eutectic melting point (170 °C) and the high electrical conductivity ($\kappa_{227\text{ }^\circ\text{C}} = 1.40 \Omega^{-1}\text{cm}^{-1}$) was used as working electrolytes at the temperature of 200 °C.³²⁾ The results obtained by cyclic voltammetric studies infer, it is not possible to recognize the anodic current peak corresponding to the ferrate(VI) production and the cathodic current peak corresponding to the ferrate(VI) reduction is easily visible. Hence, the ferrate(VI) production appeared in the potential region denoting the start of oxygen evolution.

Wet Chemical Oxidation

Wet chemical method includes the oxidation of ferric ion by sodium hypochlorite in the presence of sodium hydroxide, which can yield the sodium ferrate(VI)^{23,44,45)} but on further treatment by potassium hydroxide could give the relatively low soluble potassium ferrate(VI).⁴⁶⁾ The reactions involved are given in the following equations (2&3). The yield was *ca* 10-15% initially but the subsequent crystallization by 3M KOH can give more than 90% potassium ferrate(VI).⁴⁷⁾



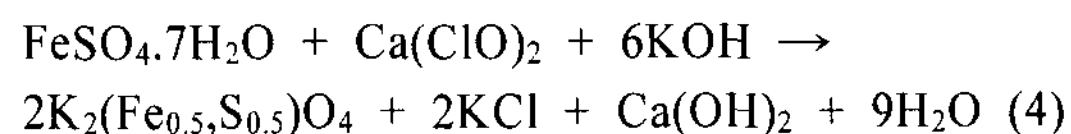
Similarly, the other alkali metal (Rb & Cs) ferrates(VI) can also be produced.⁴⁸⁾ The alkaline earth metal (Sr and Ba) ferrates(VI) were prepared by the reaction of metal chloride solution with a basic solution of potassium ferrate(VI) at 0 °C. In this process the CO₂ free water and inert atmosphere should be provided.⁴⁸⁾ Rapid filtration of strontium and barium ferrate(VI) gave a pure product.

Dry Oxidation

Sodium, potassium and cesium ferrates(VI) were prepared by dry methods. The iron oxide was treated with the oxidants (*viz.*, sodium, potassium and cesium peroxides) in presence of NaOH and O₂ at elevated temperature and pressures.⁴⁹⁻⁵³⁾

Dry synthesis at high temperature is an advantageous process because the wet preparation causes decomposition of the end product in the presence of water (Equation 1).

At the same time the dry synthesis at high temperature has got its own limitation, showing a lower thermal stability. Hence, the dry synthesis was tried at room temperature by several authors and indeed it has been pioneered by Evrard⁵⁴⁾ as treating ferrous sulphate with Ca(ClO)₂ to obtain potassium sulphatoferrate K₂(Fe_{0.5},S_{0.5})O₄. The reaction involved is given as in Equation 4:



Although this method was reported as relatively high Fe(VI) efficiency however, it may be considered as non economic since the high price of Ca(ClO)₂. From this reason Kanari et al.⁵⁵⁾ replaced the Ca(ClO)₂ by chlorine for oxidation of ferrous sulphate. The rotatory reactor was employed for the synthesis of potassium ferrate using Cl₂ as oxidizing agent and potassium hydroxide as medium and they

achieved the efficiency yield *ca* 60%. The exothermic type of reaction causes for increase of the temperature *ca* 175 °C.

CHARACTERIZATION AND DETERMINATION OF FERRATE(VI)

The efficiency and suitability of ferrate(VI) much depends upon the characterization and determination of the product hence, it seems to be worth mentioning the characterization and determination of ferrate(VI).

Characterization :

It was reported that the oxidation states of iron could be obtained by Mossbauer spectroscopy.^{48,56,57)} The characteristics of alkali and alkaline earth metal ferrates(VI) using Mossbauer spectroscopy are given in Table 1⁵⁸⁾ which obviously demonstrate that ferrate(VI) basic Mossbauer parameters, isomer shift, δ , reflecting chemical state of iron(VI), changes in very narrow limits 0.87 to 0.91 mm s⁻¹ (with respect to standard compound, α -Fe).^{21,59)} This indicates a weak influence of the outer ions on iron bounding in oxygen tetrahedron, which is main structural unit of all ferrates(VI). Consequently, oxidation properties of ferrates(VI) are expected to be same.⁶⁰⁾ Similarly, the IR spectra (1200-300 cm⁻¹) of characteristic absorption bands of FeO₄²⁻ as literature references of several ferrate(VI) salts given among others by Audette and Quail.²⁴⁾ The X-ray powder pattern obtained for solid crystals of K₂FeO₄ showed the four equivalent oxygen atoms are covalently bonded to central iron atom in +6 oxidation

state.⁶¹⁾ The tetrahedral structure was also confirmed by isotopic oxygen exchange study as performed in aqueous solutions.⁶²⁾ The reliable simulated powder XRD patterns (ICSD file No. 2876 and 32756⁶³⁾ and an experimental one (PDF File No. 25-652)⁴⁷⁾ as references for the pure substance are easily available.

Determination:

Further, the concentration of Fe(VI) is usually quantified with the 'chromic' method.⁶⁴⁾ The aqueous solution of Fe(VI) has red-violet color and the UV/Visible absorption spectra obtained at pH 9.2 in phosphate buffer gives the characteristic maxima at 510 nm and the molar absorption coefficient at this wavelength was found to be 1150 M⁻¹ cm⁻¹.^{22,65)}

Recently the group of Yoon⁶⁶⁾ has proposed spectrophotometric determination of ferrate(VI) in water by ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) as the ABTS reacts with Fe(VI) and gives a green radical cation (ABTS^{•+}) which, may be determined at 415 nm. It is to be reported that the increase in absorbance at 415 nm for ABTS^{•+} generation is linear with respect to Fe(VI) added (0.03-35 μ M) in buffered solutions (acetate/phosphate buffer at pH = 4.3) and is $3.40 \pm 0.05 \times 10^4$ M⁻¹ cm⁻¹. Further, it was suggested that this method is to be useful as can be used as a tool to determine rate constants of reactions of Fe(VI).

APPLICATIONS OF FERRATE(VI)

The importance of the ferrate lies due to its considerable and innovative applications in different fields. In aqueous phase, ferrate is

Table 1. Characteristics of ferrate (VI).⁵⁸⁾

Property	K ₃ Na(Fe ^{VI} O ₄) ₂	K ₂ Fe ^{VI} O ₄	Rb ₂ Fe ^{VI} O ₄	Cs ₂ Fe ^{VI} O ₄	K ₂ Sr(Fe ^{VI} O ₄) ₂	BaFe ^{VI} O ₄
δ mm.s ⁻¹	-0.89	-0.90-0.88	-0.89	-0.87	-0.91	-0.90
Δ , mm.s ⁻¹	0.21	0.0	0.0	0.0	0.14	0.16
H(T, K)	No magnetic ordering down to 4.2 K	14.2 \pm 2.0 (2.8 K) 14.7(0.15 K)	14.9 \pm 2.0 (2.8 K)	15.1 \pm 2.0 (2.8 K)	8.7 (2.0 K) unresolved sextet	11.8 \pm 2.0 (2.8 K)
T _N (K)		3.6-4.2	2.8-4.2	4.2-6.0	~3	7.0-8.0

reduced to ferric hydroxide precipitate and gives nascent oxygen (Equation 1). The most attractive property of the ferrate(VI) ion is its strong oxidizing ability. The redox potentials of the Fe(VI)/Fe(III) couple [$E^0(\text{FeO}_4^{2-}/\text{Fe}^{3+})$ and $E^0(\text{FeO}_4^{2-}/\text{Fe}(\text{OH})_3)$] are 2.20 and 0.72, respectively at pH 1 and 14.⁶⁷⁾ These values are significantly higher than those corresponding to the commonly used oxidants viz., Mn(VII)/Mn(IV) [$E^0(\text{MnO}_4^-/\text{MnO}_2)$ = 1.679 and 0.588 V], respectively at pH 1 and 14 or Cr(VI)/Cr(III) couples [$E^0(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+})$ = 1.33 V in acidic medium, $E^0(\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3)$ = -0.12 V, in basic medium]. The use of ferrate as oxidant instead of chromate and/or permanganate is a promising choice from the environmental point of view. One may underline that the oxidants based on chromium and manganese are corrosive, and they are irritant for the skin and for sensitive body organs such as the eyes. The use of chromium compounds as oxidant is also considered toxic for human being and environment as well.⁶⁸⁾ On the other hand ferrate reduction products are not harmful for man and environment hence find an increased attention for the application of this material in environmental remediation technology.

The strong oxidizing capacity of the ferrate (VI) initiated various possible applications in (i) the development of a high capacity battery (so called super iron battery) (ii) waste and drinking water disinfections and purification along with coagulation/flocculation. The second point received potential interest as this compound can oxidize within few seconds the stable organic/inorganic compounds present in water without forming carcinogenic or mutagenic compounds⁶⁹⁾ as it may happen while chlorination.⁷⁰⁾ The reduction product $\text{Fe}(\text{OH})_3$ is an extremely good adsorbent and coagulant for treating the waste and also having no health hazard.

The high valency and reduction of ferrate(VI) intended for an energetic and high-capacity source of cathodic charge. The possibility was explored for the development of high capacity battery referred to as super-iron battery.^{44,71-73)} Indeed the battery can provide a capacity of ca

50% higher than the conventional alkaline batteries equipped with manganese dioxide as cathode and zinc as anode.⁴⁴⁾ Hence, the manganese dioxide can be replaced with potassium and barium salt of Fe(VI) as cathodic material to achieve much enhanced efficiency.

Applications in Waste Water Treatment

The treatment of the wastewater comprises primarily two steps (i) to disinfect the harmful microorganism (e.g., bacteria & viruses) by using some disinfectant along with the degradation/oxidation of organic matters followed by (ii) the coagulation/precipitation/sedimentation/filtration of the wastes.

Disinfection must be designed as to kill the harmful microorganism and to get the water free from any harmful pathogens/microorganism. The role of chlorine, sodium hypochlorite, chlorine dioxide and ozone hydrogen peroxide²¹⁾ was well established and widely been used but the use of these chemicals poses serious environmental concerns as the use of these materials releases various carcinogenic and mutagenic by-products, which ultimately enters into the environment. Hence, in this context the suitability of ferrate (VI) was investigated much earlier in 1974⁷⁴⁾ and also used by others as well.⁷⁵⁻⁷⁸⁾ It was reported that ferrate(VI) is much effective to kill *Escherichia coli* (*E. coli*)⁷⁴⁾ and total coliforms. *f2 Coliphage* at low concentrations and a survival ratio of the virus was decreased rapidly within 10 min after it treated with ferrate(VI).⁷⁹⁾ Ferrate also inhibited the respiration of the bacterium *Sphaerotilus*; suggesting potential role in treating sludge for disinfections. Sharma et al.⁵⁹⁾ reviewed excellent properties of ferrate to kill wide variety of bacteria and virus in water and wastewater treatment processes. Recently the use of potassium ferrate (FR) 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 AS (Aluminum sulphate) and FS (Ferric sulphate) (cf Table 2).⁸⁰⁾

Table 2. Comparative performance of coagulants at optimum dose⁸⁰⁾

	AS	FS	FR	
PH	6.75-7.48	6.75-7.48	5	7
Optimum dose as ion (in mg L ⁻¹)	8	22	15	22
Optimum dose as ion (in mmol L ⁻¹)	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

AS : Aluminum sulphate ; FS : Ferric sulphate and FR : Ferrate(VI)

On the other hand due to its strong oxidizing capability it can effectively and efficiently be used for the degradation of even stable organic/inorganic matter in the wastewater. Moreover, the degradation completed within few seconds and giving out the harmless oxidizing by-products. It was reported that Fe(VI) oxidize various synthetic organic matters viz., benzene, chlorobenzene, allylbenzene and phenol etc.^{81,82)} In a line, it is fairly effective to degrade the nitrogen-containing, sulphur-containing compounds and several organic matters as well.^{21,83,84)} Similarly, De Luca et al.⁸⁵⁾ found potassium ferrate(VI) is much effective over lime in oxidizing reduced sulphur and nitrogen compounds and also mitigating odors from conditioned sludge. Inorganic contaminants viz., cyanide, ammonia, hydrogen sulphide also reported to be degraded by the ferrate(VI).^{86,87)} Chao used potassium ferrate(VI) for wastewater treatment and reported that it replaces several chemical products utilized for odor control of sludges, mainly aggressive odors caused by ammonia and sulphides, through the formation of precipitates with iron compounds. Ferrate(VI) applied to sludge also has the double effect of transforming ammonia into nitrates, such that this product takes the place of sulphates, acting as an electron acceptor, thus preventing the development of further odors when biosolids are utilized.⁸⁵⁾

Several other reports also stated that hydrogen sulphide, mercaptans and amines can be degraded efficiently by ferrate(VI)^{83,88-90)} giving out the non-toxic by-products (e.g., Equation 5; sulfide degraded into sulphate⁹¹⁾). The reaction

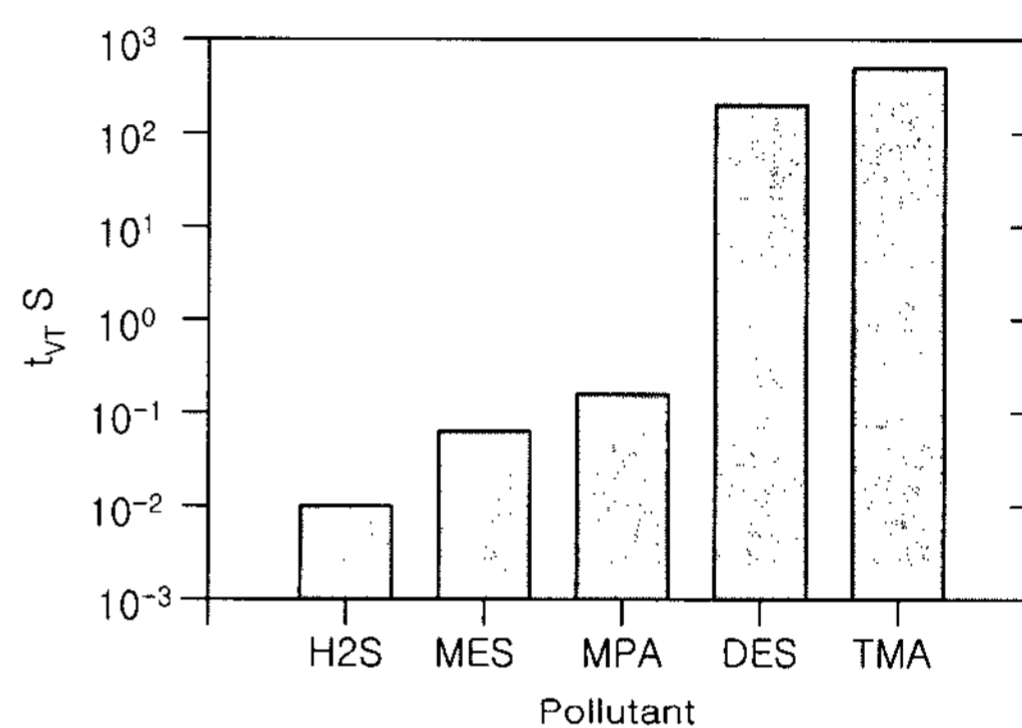
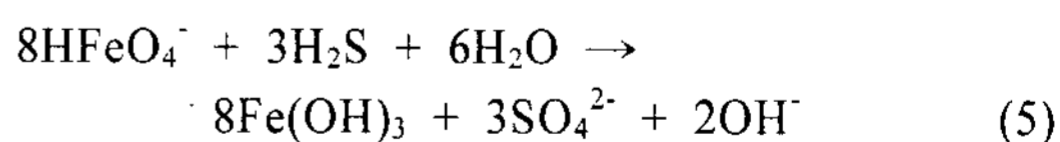


Figure 1. Half-lives of the reactions between Fe(VI) (500 μM) at pH 9 and 25 °C. MES - 2-mercaptoethanesulfonic acid; MPA - 2-mercaptopropionic acid; DES - diethylsulphide; TMA - trimethylamine.

rate law (first order rate law with respect to both reactants) and observed rate constants at pH 9 were used to determine the half-lives of the oxidation processes (Figure 1). Figure shows the half-lives of the oxidation process, which varies from milli seconds to seconds.

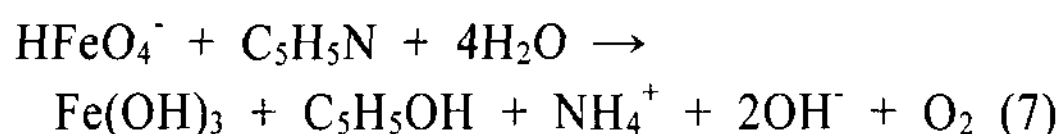
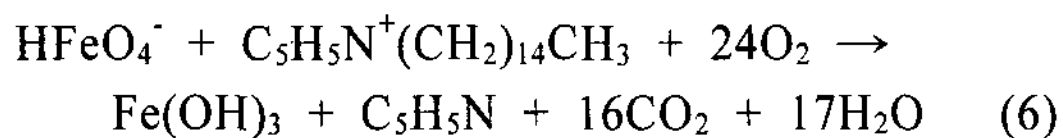


The sulfamethoxazole (contains nitrogen and sulphur atoms having benzene and five membered rings), an antibiotic drug was investigated for the oxidation with ferrate(VI) at different pH (7.0 to 9.5) at 25 °C. 1:1 stoichiometry of ferrate(VI) and sulfamethoxazole was observed and the rate decreases with the increase in pH and it found to be dependent to the protonation of ferrate(VI) ($\text{HFeO}_4^- \rightleftharpoons \text{H}^+ + \text{FeO}_4^{2-}$; $\text{pK}_{a,\text{HFeO}_4^-} = 7.23$) and sulfamethoxazole ($\text{BH}^+ \rightleftharpoons \text{H}^+ + \text{B}$;

$pK_{a,HB} = 5.7$). Also the reaction follows first order rate law with respect to the reactants.⁹²⁾

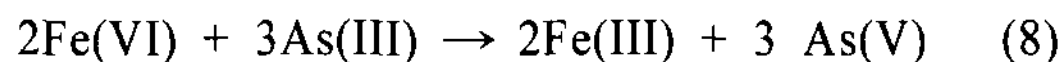
Several reports mentioned about the oxidation of organic compounds *viz.*, cystiene⁹³⁾, 2-mercaptoethansulphonate⁹⁴⁾, thiourea⁹⁵⁾, benzenesulfinat⁹⁶⁾, 1,4-thioxane⁹⁷⁾, aniline⁸³⁾, benzylamine⁹⁸⁾, glycolaldehyde, formaldehyde, formic acid, methanol⁹⁹⁾, p-toluidine⁸³⁾ etc. and few inorganic compounds *viz.*, superoxide ion, hydrogen peroxide¹⁰⁰⁾, hydrazine¹⁰¹⁾, hydroxylamine¹⁰²⁾, cyanide⁸⁶⁾, ammonia¹⁰³⁾ etc. It is to be reported that all reaction processes followed the second order rate law and their rate constant values were well summarized by Lee et al.²²⁾ Similarly, the phenolic endocrine-disrupting chemicals (EDCs) and phenols were effectively oxidized by ferrate(VI) as studied for natural and waste water samples.¹⁰⁴⁾

The surfactants, as mentioned previously, are not directly toxic but they inhibit both settling of floating particles and dissolution of atmospheric oxygen into natural waters, causing several environmental concerns. The strong oxidizing capability of ferrate(VI) was prompted to investigate the possible oxidation of surfactants particularly the CPC (cetylypyridinium chloride, $C_5H_5N^+(CH_2)_{14}CH_3 \cdot H_2O \cdot Cl^-$).¹⁰⁵⁾ The study carried out at pH 9.2 and reported that Ferrate(VI) can remove CPC completely and the TOC (total organic carbon) also reduced to 95%. Results indicate that the aliphatic chain of CPC is mineralized to inorganic carbon in the initial reaction of ferrate(VI) with CPC gives ammonia, which suggests the ring opening in the remaining organic molecule. This molecule may also react with ferrate(VI) to result in complete destruction of CPC (*cf* Equations 6 & 7). Hence, the ferrate(VI) can degrade the CPC completely and give relatively non-toxic by-products.



Application of ferrate(VI) in the removal of

arsenic was first investigated by Lee et al.¹⁰⁶⁾ They reported that two moles of Fe(VI) were required to oxidize 3 moles of As(III) into As(V) and the final product of Fe(VI) was confirmed to be Fe(III) (Equation 8). The second order reaction process completed within few seconds only:



Further, they applied the same procedure for the removal of arsenic from river water (Nakdong River in Korea) and find out the efficiency of ferrate(VI) and also the produced Fe(III) (commonly used coagulant for arsenic) in terms of their arsenic removal from water. It was reported that the practical efficiency of the arsenic removal can be achieved by addition of small amounts of Fe(III) (a supplement coagulant).

Moreover the decomposition byproduct (Fe(III)) generated from ferrate(VI) reduction exhibits valuable coagulating properties, which improves the efficiency of the entire waste treatment and found to be environmentally friendly as due to its non-toxic behavior.^{21,83,107-109}

CONCLUSIONS

Ferrate(VI) is found to be potentially applicable in wastewater treatment technology as due to its strong oxidizing tendency. It can effectively and efficiently oxidize even stable organic/inorganic matters along with variety of pathogens viruses etc. and the by-products obtained followed by the oxidation are non-toxic hence it can be used as a 'green chemical' for such studies. Also the reduction of ferrate(VI) into Fe(III) in the form of $Fe(OH)_3$ at alkaline pH is found to be fairly good coagulant/precipitant and adsorbent, hence, the single chemical serves as an oxidant, disinfectant, coagulant, precipitant, adsorbent etc. properties.

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