

Ferrates (iron(VI) and iron(V)): Environmentally friendly oxidants and disinfectants

Virender K. Sharma, Futaba Kazama, Hu Jiangyong and Ajay K. Ray

ABSTRACT

Iron(VI) and iron(V), known as ferrates, are powerful oxidants and their reactions with pollutants are typically fast with the formation of non-toxic by-products. Oxidations performed by Fe(VI) and Fe(V) show pH dependence; faster rates are observed at lower pH. Fe(VI) shows excellent disinfectant properties and can inactivate a wide variety of microorganisms at low Fe(VI) doses. Fe(VI) also possesses efficient coagulation properties and enhanced coagulation can also be achieved using Fe(VI) as a preoxidant. The reactivity of Fe(V) with pollutants is approximately 3–5 orders of magnitude faster than that of Fe(VI). Fe(V) can thus be used to oxidize pollutants and inactivate microorganisms that have resistance to Fe(VI). The final product of Fe(VI) and Fe(V) reduction is Fe(III), a non-toxic compound. Moreover, treatments by Fe(VI) do not give any mutagenic/carcinogenic by-products, which make ferrates environmentally friendly ions. This paper reviews the potential role of iron(VI) and iron(V) as oxidants and disinfectants in water and wastewater treatment processes. Examples are given to demonstrate the multifunctional properties of ferrates to purify water and wastewater.

Key words | ferrate, iron(VI), iron(V), oxidation, disinfectant, water

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INTRODUCTION

Access to abundant clean water is a serious issue affecting the physical and economic health of world communities. Worldwide, water and wastewater treatment processes are practised to prevent disease and to renew precious fresh water resources. This strategy is especially critical in many arid and semi-arid regions of the world where recycled or treated water is often the only source of potable water. According to the World Health Organization (WHO) estimates, more than 1 billion people are without access to adequate sources of drinking water. Many people in the world suffer illness and death each year due to drinking water contamination (Rose *et al.* 2000). Water not fully disinfected has caused recent outbreaks of *Escherichia coli*-induced gastroenteritis in Walkerton, Ontario (2000), cryptosporidiosis in Milwaukee, Wisconsin (1993), and cholera in Peru (1991) (Richardson *et al.* 2002; Hunter 2003).

Filtration and disinfection have long been accepted as treatment methods to protect public health. However,

filtration is considered a poor barrier for removing viruses or spores, which are quite small (Rose 2002). Thus, filtration may not achieve a 99% reduction in contamination level. Some other species such as anthrax and *Cryptosporidium* resist chlorination, a commonly used disinfection method (Burrows & Renner 1999; Craun & Calderon 2001; Rose 2002). Moreover, chlorination creates and leaves disinfectant by-products (DBP) in treated water. Trihalomethanes (THMs) are examples of DBPs that have been shown to be carcinogenic in rodents (Boorman *et al.* 1999). Epidemiological studies suggest some correlation between the consumption of chlorinated drinking water and the occurrence of bladder, colon and rectal cancer (Richardson 2003).

Alternative oxidants such as bromine, iodine, chlorine dioxide, ozone and chloramines have been considered to replace chlorine. However, they also form a wide range of by-products, some of which are toxic to the aquatic

environment and to human populations (Hass *et al.* 1999; Panagioti & Graham 2002). Treatment success using these disinfectants depends on the source water conditions such as pH, and the existing levels of bromide, iodide and natural organic matter (NOM). For example, ozone can reduce levels of THMs and halo acetic acids (HAAs), but it can form the potent carcinogenic bromate ion by reacting with bromide present in water (Gunten 2003; Richardson 2003). Recent research suggests that treatment with monochloroamine produces N-nitrosodimethylamine (NDMA), a suspected human carcinogen (Mitch & Sedlak 2002). This research has caused alarm in the treatment industry because the main purpose of monochloroamine application as a disinfectant is to avoid toxic by-products.

The use of ultraviolet (UV) radiation for water and wastewater disinfection has increased in recent years. UV radiation's advantage is that it does not produce DPBs from chlorine residuals and UV acts against bacteria, viruses and protozoa. However, the inactivation of bacteria by UV can be partially reactivated with near-UV light or visible light (Kashimada *et al.* 1996). Recent studies have shown that reactivation is more prominent when water is disinfected at a low dose of UV (Zimmer *et al.* 2003; Otaki *et al.* 2003). Improvements in UV technology components including reactor designs and lamps may increase its effectiveness to disinfect water. A new technology that effectively treats a wide range of contaminants, including microorganisms, is needed. This technology should also remove unconventional and emerging microorganisms. Furthermore, viruses attached to other organisms or particles need more thorough disinfection (Hass 2002; Rose 2002). Finally, this technology should not only remove all toxins and contaminants of concern, but also form no toxic side reactions or by-products.

Ferrates, iron(VI) (Fe (VI)) and iron(V) (Fe (V)), are environmentally friendly treatment ions that can meet these new challenges confronting the water industry. In this paper, the potential role of Fe(VI) and Fe(V) as oxidants and disinfectants in water and wastewater treatment processes is reviewed.

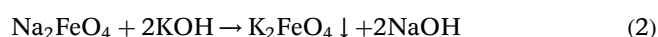
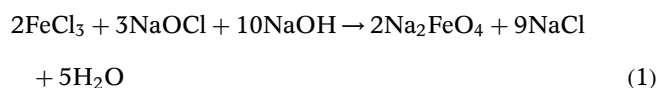
IRON(VI)

Iron commonly exists in the +2 and +3 oxidation states; however, in a strong oxidizing environment, higher

oxidation states of iron such as +4, +5 and +6 can also be obtained (Rush & Bielski 1986; Jeannot *et al.* 2002). In recent years, the +6 oxidation state of iron, ferrate (Fe(VI)), has received much attention because of its usefulness in green organic synthesis, 'super-iron' batteries and wastewater treatment processes (Delaude & Laszlo 1996; Sharma 2002a; Licht *et al.* 2002). In the laboratory, Fe(VI) can be produced by three types of synthetic techniques. These techniques are briefly described below.

Wet synthesis

This method produces sodium ferrate(VI) (Na₂FeO₄) from the reaction of ferric chloride with sodium hypochlorite in the presence of sodium hydroxide (Thompson *et al.* 1951; Schreyer *et al.* 1953; White & Franklin 1998). Potassium hydroxide is added to a sodium ferrate(VI) solution to precipitate potassium ferrate(VI) (K₂FeO₄). The basic reactions are as follows:



This procedure produces a 10–15% yield of potassium ferrate(VI) and many separation steps are required to obtain solid potassium ferrate(VI) of more than 90% purity.

Dry synthesis

The formation of Fe(VI) in the system Fe₂O₃-NaOH-Na₂O₂-O₂ at different temperatures has been reported (Scholder *et al.* 1956, Scholder 1962). The yield of this method is usually less than 50%. The fusion of Na₂O₂ with Fe₂O₃ at a molar ratio [Na]:[Fe] = 4:1 under dry oxygen conditions at 370 °C yields sodium ferrate(VI) (Perfiliev 2002). The dry synthesis of potassium ferrate(VI) from dehydrated ferrous sulphate has also been reported (Neveux *et al.* 1999).

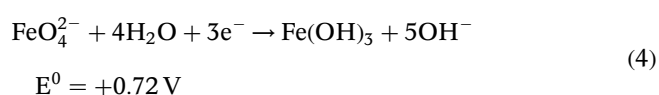
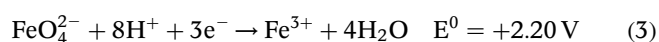
Electrochemical synthesis

In an electrochemical method, anodic iron in NaOH solution is oxidized to Fe(VI) by setting an appropriate anode potential (Denvir & Pletcher 1996; Bouzek *et al.*

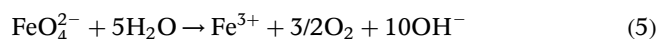
2000). This approach is appealing for the synthesis of Fe(VI) because it uses electrons as 'clean' reactants and also produces a pure dissolved Fe(VI) product. However, this method has two disadvantages: (i) relatively low yield (<50%) of the process and (ii) problems connected with separation of the product in a solid form (Lescuras-Darrou *et al.* 2002). The latter point has to be solved in order to provide a Fe(VI) product of sufficient stability, which also does not elevate the pH of water in the treatment processes. Recently, mixed NaOH-KOH solutions were used to synthesize solid potassium ferrate(VI) with appreciable yields (>50%) (Lapicque & Valentine 2002). In acidic media, electrochemical generation of Fe(VI) has also been suggested (Lee *et al.* 2002).

IRON(VI) OXIDATION OF POLLUTANTS

Fe(VI) is a powerful oxidizing agent in aqueous media, which can be seen from the reduction potentials of reactions (3) and (4) in acidic and alkaline solutions, respectively (Wood 1958).



Under acidic conditions, the redox potential of the Fe(VI) ion is the highest of any other oxidant used in water and wastewater treatment processes. The spontaneous oxidation of Fe(VI) in water forms molecular oxygen (Goff & Murmann 1971).



Another by-product of Fe(VI) is non-toxic, Fe(III), making Fe(VI) an environmentally friendly oxidant (Waite 1978, 1979; Waite & Gray 1984; Carr *et al.* 1985; Lee & Chen 1991; Lee & Gai 1993; White & Franklin 1998; Johnson & Sharma 1999; Jiang *et al.* 2001; Read *et al.* 2001, 2003; Jiang & Lloyd 2002). Moreover, the ferric oxide produced from Fe(VI) acts as a powerful coagulant that is suitable for the removal of metals, non-metals, radionuclides and humic acids (Potts & Churchwell 1994; Stupin & Ozernoi 1995; Neveux *et al.*

1999; Jiang & Wang 2003a). Fe(VI) is therefore an efficient chemical for recycling and reusing water and wastewater.

In our laboratory, kinetics and stoichiometric measurements have been carried out for the oxidation of sulphur- and nitrogen-containing pollutants by Fe(VI). The pollutants studied were hydrogen sulphide (H_2S), thiourea (TU; NH_2CSNH_2), thioacetamide (THA; CH_3CSNH_2), cyanide (HCN) and thiocyanate (SCN^-) (Sharma *et al.* 1997, 1998a, b, 1999, 2000, Sharma 2002a). The reactions of Fe(VI) with pollutants were found to be first order for each reactant. The reaction rate constants were determined as a function of pH and the rate of the reaction increases with a decrease in pH: for example, the oxidation of hydrogen sulphide by Fe(VI) as shown in Table 1. This phenomenon is due to the faster reaction rates of the protonated form of Fe(VI) (HFeO_4^-) versus the ionized form (FeO_4^{2-}).



$$\text{pK}_{\text{a,HFeO}_4} = 7.23 \quad (\text{Sharma } et al. 2001a)$$

The decrease in fraction of HFeO_4^- ($\alpha(\text{HFeO}_4^-)$) with increase in pH from 7 to 11 decreased the rate constants of the reaction (Table 1). The fraction of the deprotonated form of Fe(VI) ($\alpha(\text{FeO}_4^{2-})$) remains relatively constant from pH 9 to 11, while the rates of the reaction still decrease. This further demonstrates that reaction rates depend on the concentration of HFeO_4^- in the solution.

The reaction rate law and the observed rate constants at pH 9 were used to determine the half-lives of the oxidation processes (Figure 1). The half-lives of the reactions vary from milliseconds to seconds; sulphur-containing pollutants tend to react faster with Fe(VI) than nitrogen-containing pollutants. The removal of the most reactive pollutant, H_2S ,

Table 1 | The fractions of Fe(VI), rate constants (k), and half-lives ($t_{1/2}$) of oxidation of hydrogen sulphide by Fe(VI)

pH	$\alpha(\text{HFeO}_4^-)$	$\alpha(\text{FeO}_4^{2-})$	$k (\text{M}^{-1} \text{s}^{-1})$	$t_{1/2} (\text{ms})$
7.0	0.6294	0.3706	7.80×10^6	0.26
9.0	0.0167	0.9833	2.08×10^5	9.62
11.0	0.0002	0.9998	2.95×10^3	679

M = Concentration in moles per litre.
s = time in seconds.

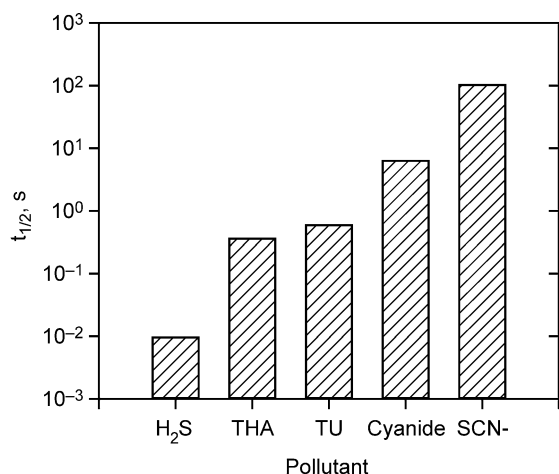


Figure 1 | Half-lives of the reactions between Fe(VI) (500 μ M) and pollutants (100 μ M) at pH 9 and 25 °C (THA, thioacetamide; TU, thiourea).

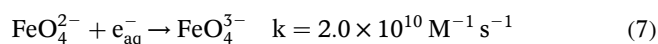
by Fe(VI) can be accomplished in milliseconds while removal of the least reactive pollutant, thiocyanate, would take seconds. It should be pointed out that the reaction rates are pH dependent; thus, so are the half-lives of the reactions. Destruction of pollutants by Fe(VI) resulted in relatively non-toxic by-products (Table 2). Sulphur groups present in H₂S, thioacetamide and thiourea became sulphate, and cyanide was converted to cyanate and nitrite.

Preoxidation by Fe(VI) is advantageous in coagulation of surface waters (Ma & Liu 2002a). In the preoxidation process, Fe(VI) destroys the organic coating on the particle and aids in coagulation. The floc size of the coagulant was larger in a Fe(VI) preoxidation process than that of an alum coagulant alone. This was particularly noticeable in organic-rich waters in which alum was less effective in

reducing turbidity (Ma & Liu 2002a). In a separate study, the reduction of fulvic acid was more effective with the combination of Fe(VI) and polyaluminium chloride or ferric chloride (Qu *et al.* 2003).

IRON(V) PRODUCTION

Solid phase synthesis of Fe(V) has been performed (Temple & Thickett 1973). Iron in the FeO₄³⁻ form has been suggested using X-ray studies of isolated crystals of the solid. In aqueous solution, Fe(V) was conveniently generated in aqueous solution by pulse radiolysis in which Fe(VI) reduces to Fe(V) by radicals such as e_{aq}⁻ at near diffusion-controlled rates (reaction 7) (Bielski & Thomas 1987).



Recent work in our laboratory on the heterogeneous photocatalytic reduction of Fe(VI) in UV-irradiated titanium dioxide (TiO₂) suspensions suggest the formation of Fe(V) by the photoreduction of Fe(VI) with a conduction band electron (e_{cb}⁻) at TiO₂ surfaces (reaction 8).



Experiments on the photocatalytic reduction of Fe(VI) were conducted at two different TiO₂ suspension doses as a function of Fe(VI) concentration at pH 9.0 (Sharma *et al.* 2001c, Sharma 2004). The photoreduction of Fe(VI) in these suspensions occurred at a faster rate than in the absence of TiO₂. Additionally, photoreduction was greater at higher TiO₂ doses. The photoreduction of Fe(VI) to Fe(OH)₃ at TiO₂

Table 2 | Oxidation products in the reaction of Fe(VI) with pollutants at pH 9.0

Pollutant (P)	Stoichiometry Fe(VI): P	Product(s)
Hydrogen sulphide	8 : 3	Sulphate (SO ₄ ²⁻)
Thioacetamide	8 : 3	Acetamide (CH ₃ CONH ₂), sulphate (SO ₄ ²⁻)
Thiourea	8 : 3	Urea (NH ₂ CONH ₂), sulphate (SO ₄ ²⁻)
Cyanide	1 : 1	Cyanate (CNO ⁻), nitrite (NO ₂ ⁻)
Thiocyanate	4 : 1	Cyanate (CNO ⁻), nitrite (NO ₂ ⁻), sulphate (SO ₄ ²⁻)

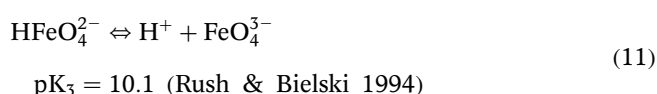
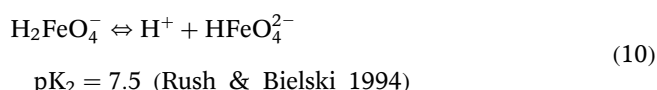
surfaces can be expressed by reaction (9) (Sharma *et al.* 2003).



IRON(V) OXIDATION OF POLLUTANTS

Studies were made on the kinetics of Fe(V) with pollutants using a pre-mix pulse radiolysis technique (Sharma & O'Connor 2000, Sharma *et al.* 2001b, 2002; Sharma, 2002b). Similar to the kinetics of Fe(VI), the reactions with Fe(V) were first order for each reactant. The rate constants for the reactivity of Fe(V) with thiourea, cyanide and thiocyanate are given in Table 3. Fe(V) is approximately three orders of magnitude more reactive towards these pollutants than Fe(VI) (Table 3). The higher reactivity may be due to the partial free-radical character of Fe(V) ($\text{Fe}^{\text{V}} = \text{O} \leftrightarrow \text{Fe}^{\text{IV}} - \text{O}^\cdot$). Therefore, Fe(V) is a more powerful oxidant than Fe(VI).

Pollutant oxidation rates by Fe(V) increase with a decrease in pH (Sharma *et al.* 2002). This is related to the faster reaction rates of the protonated form of Fe(V) (HFeO_4^{2-}) compared with the nonprotonated form (FeO_4^{3-}) (Equations 10 and 11).



Thus, oxidation rates depend on the protonation of Fe(V) (Table 3). The half-lives of the oxidation of pollutants by Fe(V) would also be pH dependent.

Table 3 | Reaction rate constants ($\text{M}^{-1}\text{s}^{-1}$) for reactions of pollutant with Fe(VI) and Fe(V) (k , $\text{M}^{-1}\text{s}^{-1}$) at 25°C

Pollutant	Fe(V)	Fe(VI)	Fe(V)	Fe(VI)
	pH = 10.1		pH = 12.4	
Thiourea	2.10×10^5	2.00×10^2	8.10×10^3	3.00×10^1
Cyanide	6.00×10^5	5.00×10^1	2.00×10^4	9.00×10^{-1}
Thiocyanate	3.63×10^3	1.18×10^0	–	–

The Fe(VI)-TiO₂-UV system can also be applied to oxidize pollutants (Sharma *et al.* 2003). Studies involving photocatalytic oxidation of ammonia, cyanate and fulvic acid have been initiated. These pollutants react sluggishly with either aqueous Fe(VI) solution or illuminated TiO₂ suspensions individually. The photocatalytic oxidation of ammonia was found to be approximately three times faster in the presence of Fe(VI) than with no Fe(VI) in the solution mixture (Sharma *et al.* 2001c). Fe(V) as an intermediate explained the faster photocatalytic oxidation of ammonia in the presence of Fe(VI). The photoreduction rate of Fe(VI) also increased in the presence of ammonia in the solution. A higher reduction rate of Fe(VI) was noted in the presence of cyanate and fulvic acid (Sharma *et al.* 2003).

IRON(VI) AND IRON(V) APPLICATIONS IN DISINFECTION

Fe(VI) as a disinfectant replacement for chlorine has been investigated for the last three decades (Murmah & Robinson 1974; Gilbert *et al.* 1976; Waite 1979; Schink & Waite 1980; Kato & Kazama 1983, 1984, 1990, 1991; Kazama 1989, 1994, 1995; Karaatli 1998; Tüzün *et al.* 1999; Jiang *et al.* 2002, Jiang & Wang 2003b). Fe(VI) can achieve disinfection at relatively low dosages over a wide range of pH. Moreover, the application of Fe(VI) does not produce any mutagenic/carcinogenic by-products (De Luca *et al.* 1983). The role of Fe(VI) in inactivating microorganisms and the mechanism of various disinfection processes are summarized below.

Bacteria

Many workers have tested the removal of total and fecal coliform by Fe(VI) (Waite 1979; Jiang *et al.* 2002). Fe(VI) treatment of water sources collected worldwide can achieve more than 99.9% kill rate of total coliforms (Table 4). Source water characteristics such as pH, suspended solids, chemical oxygen demand (COD) and NH₃-N of the tested samples were all different. The results in Table 4 indicate that the dosages of Fe(VI) required for complete destruction of coliforms varied with the initial numbers of microorganisms in water before treatment with Fe(VI).

Table 4 | Disinfection of water and wastewater by potassium ferrate(VI) that achieved more than 99.9% reduction of total coliform bacteria

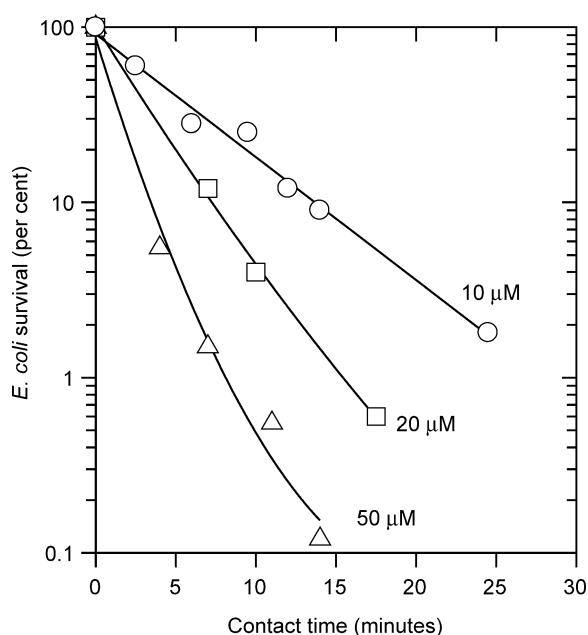
Source	pH	Suspended solids (mg l ⁻¹)	NH ₃ -N (mg l ⁻¹)	COD (mg l ⁻¹)	Total coliform (MPN ml ⁻¹) (prior to disinfection)	Doses as Fe in K ₂ FeO ₄ (mg l ⁻¹)	Reference
Lake Water, UK	3.5–7.5	–	–	–	$1.2–2.1 \times 10^2$	0.5	Jiang <i>et al.</i> 2002
Lake Water, Turkey	6.5	15.6	0.295	43.4	50×10^4	2.5	Karaatli 1998
Wastewater, Turkey	6.8	158.3	29	151	7.0×10^{10}	12.5	Karaatli 1998
Sewage Plant	6.8	109.6	21.0	51.2	1.4×10^5	5.1	Kato & Kazama 1991
Water Drain	7.4	121.6	0.40	47.3	3.9×10^4	3.4	
River Water1	7.3	19.8	6.40	14.5	4.1×10^4	3.1	
River Water2	7.4	6.20	8.70	5.00	1.1×10^3	2.3	
River Water3, Japan	7.3	2.40	0.20	1.20	2.1×10^2	0.6	
Secondary effluents, USA	8.0	18.0	2.5	–	2.5×10^5	3.7	Waite 1979
	90.0	3.5					

Fe(VI) disinfection was also examined for *Escherichia coli*, an indicator organism of fecal contamination (Waite 1979; Kato & Kazama 1991; Jiang & Wang 2003b). The disinfection properties of Fe(VI) for *E. coli* at three different doses are demonstrated in Figure 2. Fe(VI) is effective in killing *E. coli* (Waite 1979). However, contact time of effectiveness depends on dose rate (Figure 2). Another study reported Fe(VI) disinfection of *E. coli* (Kato & Kazama 1984). Suspended solids such as clay and organic particulates did not influence biocidal effects of Fe(VI); however, the killing of *E. coli* depended on water buffering capacity.

Recently, Jiang & Wang (2003b) performed disinfection studies with both Fe(VI) and hypochlorite for *E. coli* in water. Comparatively, the disinfection by Fe(VI) was less affected by the solution pH than hypochlorite disinfection. No pH pre-adjustment may be needed in using Fe(VI). Relatively higher doses and contact times were required for hypochlorite disinfection than for Fe(VI). Performance of Fe(VI) was superior to hypochlorite in killing *E. coli*.

The respiration of bacterium *Sphaerotilus* in the presence of K₂FeO₄ has been studied in detail (Kato & Kazama 1990; Kazama 1989). This bacterium causes

filamentous bulking in activated sludge. Fe(VI) strongly inhibits the exogenous respiration of the bacterium *Sphaerotilus*. Studies demonstrated that the penetration into the

**Figure 2** | Inactivation of *E. coli* exposed to K₂FeO₄ at pH 8.0 and 27 °C (reproduced from Waite 1979).

cells is important in the respiratory inhibition caused by K_2FeO_4 . The extent of penetration into the cells is closely related to inhibition of endogenous respiration. K_2FeO_4 thus inhibits both exogenous and endogenous respiration of *Sphaerotilus*.

Studies suggest that dehydrogenase activity is one of the most important factors involved in inhibition of endogenous respiration of *Sphaerotilus* (Kazama 1994, 1995). Figure 3 shows dehydrogenase activity at different amounts of K_2FeO_4 . Dehydrogenase activity of *Sphaerotilus* was decreased by more than 85% by K_2FeO_4 . Inhibition of dehydrogenase activities at pH 6.2 and pH 7.0 were similar. The reactivation of the enzyme inhibited by Fe(VI) ion was also carried out by adding 2-mercaptoethanol (MCE). Molar ratios (MCE: K_2FeO_4) from 9 to 91 restored enzyme activity up to 79% at a lower dose of K_2FeO_4 (1.6 mg Fe). However, restorations at higher doses of 3.11 and 7.9 mg Fe were limited. The inhibition of dehydrogenase activity of *Sphaerotilus* is possibly caused by inactivation of SH-radicals in the enzyme molecule. It is likely that Fe(VI) and/or intermediates, Fe(V) and Fe(IV), of FeO_4^{2-} decomposition penetrate the sheaths and cell walls to inactivate the SH-radicals in the dehydrogenase molecule. These possible mechanistic steps of *Sphaerotilus* inactivation by Fe(VI) need further exploration.

Franklin (1998) has tested the disinfecting power of sodium ferrate(VI) on spore-forming bacteria (Figure 4). Aerobic spore-formers can be reduced up to 3-log units

while sulphite-reducing clostridia were effectively killed by Fe(VI). Both bacteria were resistant to chlorination. Other bacterial species that are susceptible to Fe(VI) are *Bacillus cereus*, *Streptococcus bovis*, *Staphylococcus aureus*, *Shigella flexneri*, *Streptococci faecalis* and *Salmonella typhimurium* (Murmman & Robinson 1974; Gilbert *et al.* 1976).

The oxidation of *E. coli* DNA polymerase-I by Fe(VI) was performed (Basu *et al.* 1987). Fe(VI) treatment resulted in loss of polymerization and 3'-5' exonuclease activity and thus the irreversible inactivation of the enzyme. A large fragment of *E. coli* DNA polymerase-I was modified by Fe(VI) through oxidation at a minimum of five sites. Fe(VI) can also inactivate murine leukaemia virus reverse transcriptase (MuLV RT), which is expressed in *E. coli* (Kotewicz *et al.* 1985). MuLV RT contains both DNA polymerase and RNase H activities. Treatment by Fe(VI) resulted in loss of both polymerase and nuclease activities (Reddy *et al.* 1991). In the oxidation process, there was loss of template-primer binding function in MuLV RT. The probable sites of Fe(VI) oxidation were Lys-285 of polymerase domain and Cys-635 of RNase H domain.

Degradation of deoxyribonucleosides by potassium ferrate(VI) was examined (Stevenson & Davies 1995). Experiments were conducted on the reactivity of Fe(VI) with four common 2'-deoxyribonucleosides, deoxyadenosine (dA), deoxyguanosine (dG), deoxycytidine (dC) and thymidine (dT), at pH 8. The most readily oxidized

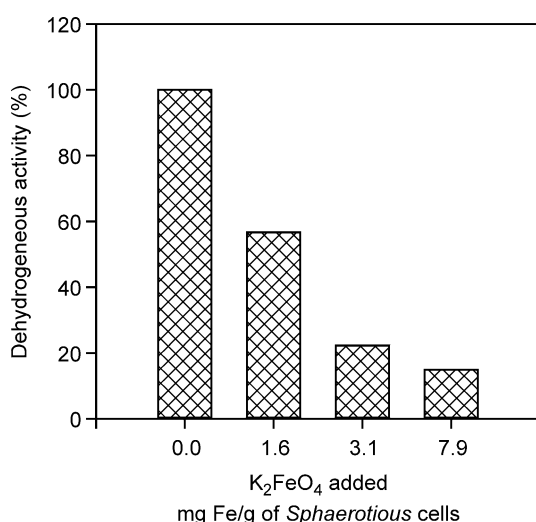


Figure 3 | Inhibition of dehydrogenase activity of *Sphaerotilus* by K_2FeO_4 .

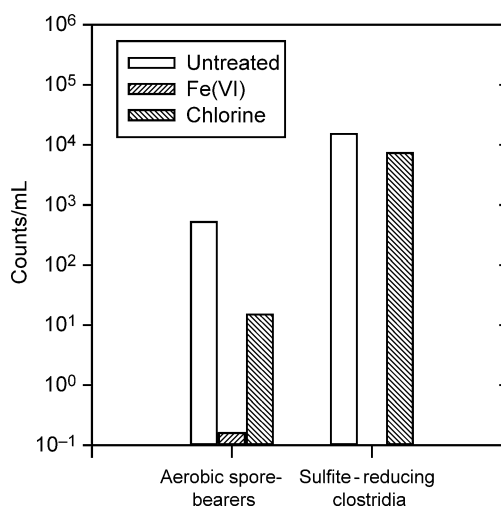


Figure 4 | Disinfection of river water by Fe(VI) over 30 minutes' contact time (sodium ferrate(VI), 2 mg l⁻¹ as Fe; hypochlorite, 3.5 mg l⁻¹ chlorine).

deoxyribonucleoside was dG; however, dA showed resistance. The intermediate reactivity for dC and dT was found. At 10: 1 molar ratio of Fe(VI) to deoxyribonucleoside, the degradations were dG(100%), dC(62%), dT(25%) and dA(13%). The results suggested that Fe(VI) probably oxidizes G and T bases in DNA, producing lesions that are unstable at alkaline pH. This process may ultimately cause DNA chain cleavage through a mechanism in which base loss is followed by β -elimination at the abasic site. The experimental studies on Fe(VI) oxidation of DNA further support the role of Fe(VI) as an alternative disinfectant for water treatment.

Viruses

Studies on the effectiveness of ferrate(VI) on virus destruction and removal have been reported (Schink & Waite 1980; Kazama 1994, 1995). The viruses tested were *Enterobacteria phage f2* and *Enterobacteria phage Q β* , which belong to the family *Leviviridae*. The results have shown that Fe(VI) rapidly inactivates virus *f2* at low concentrations and pH 6–8 in water and secondary effluents (Schink & Waite 1980). The disinfection process did not follow first-order kinetics. Virus *Q β* was also effectively inactivated by Fe(VI) in a phosphate buffer at pH 6, 7 and 8 (Kazama 1994, 1995). The inactivation rate increased with a decrease in pH.

The rate of inactivation can be expressed by the Chick-Watson Law (Equation 12).

$$\log(N_t/N_0) = -K' C^n t^m \quad (12)$$

where N_t and N_0 are the virus concentration at time t and zero, respectively; K' is indicative of the inactivation rate of virus and n and m are indicators of the relative effects of concentration and exposure time (t), respectively. A linear relationship was found between $\log(\log(N_t/N_0))$ and $\log(t)$ (Kazama 1995). The obtained values of K' were pH dependent while $n = 0.54 \pm 0.04$ did not vary with pH. Values of K' increase from 0.42 to 2.0 $L^n/mg^n \min^m$ as pH decreases from 8.0 to 6.0 (Kazama 1994). This pattern in K' is mostly related to the fraction of reactive protonated form of Fe(VI) ($\alpha(HFeO_4^-)$) in solution (Figure 5). A reasonably linear relationship between K' and $\alpha(HFeO_4^-)$ (Figure 5) further suggests the major role of protonated Fe(VI) in inactivating viruses in water.

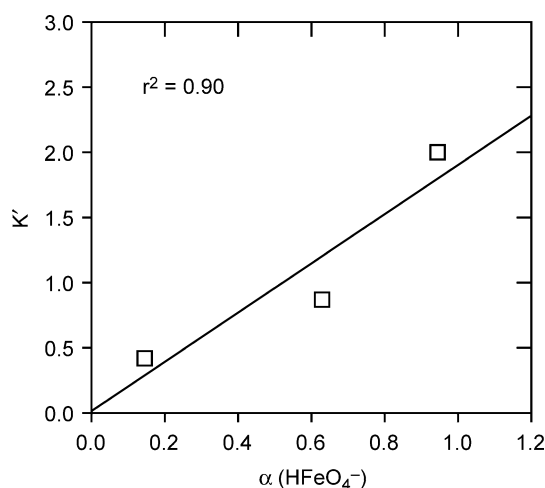


Figure 5 | Inactivation of bacteriophage by Fe(VI).

Algae

Enhanced coagulation of algae was found when water was pretreated with potassium ferrate(VI) (Ma & Liu 2002b). Jar tests for removal of algae by alum in lake water and cultured solution were conducted (Ma & Liu 2002a) (Figure 6). In both waters, algae removal by alum increased significantly with the use of low dosages of Fe(VI) in a short 1 minute preoxidation time. Enhanced coagulation of algae increased with increasing Fe(VI) at all alum doses. However, the percentage of algae removal was more pronounced in lake water than cultured water at all dosages of alum. The difference in quality of two waters may cause two levels of enhanced coagulation of algae. Liu & Ma (2002) also showed that humic acids present in water greatly influenced the coagulation of algae by alum. Pretreatment with Fe(VI) reduces the adverse impact of humic acid on the coagulation of algae.

Microcystins

There is growing concern in the environmental community regarding toxin production during cyanobacterial blooms in water bodies. Microcystins are the most commonly occurring toxins produced by cyanobacteria. Increases in eutrophication activities cause these cyanobacterial blooms. When blooms senesce, cyanobacteria cell lyses release heptatoxins into the surrounding water. Some treatment processes may also cause cell disruption and increase the levels of toxins in water. Adverse health effects of microcystins include tumour-promoting activity

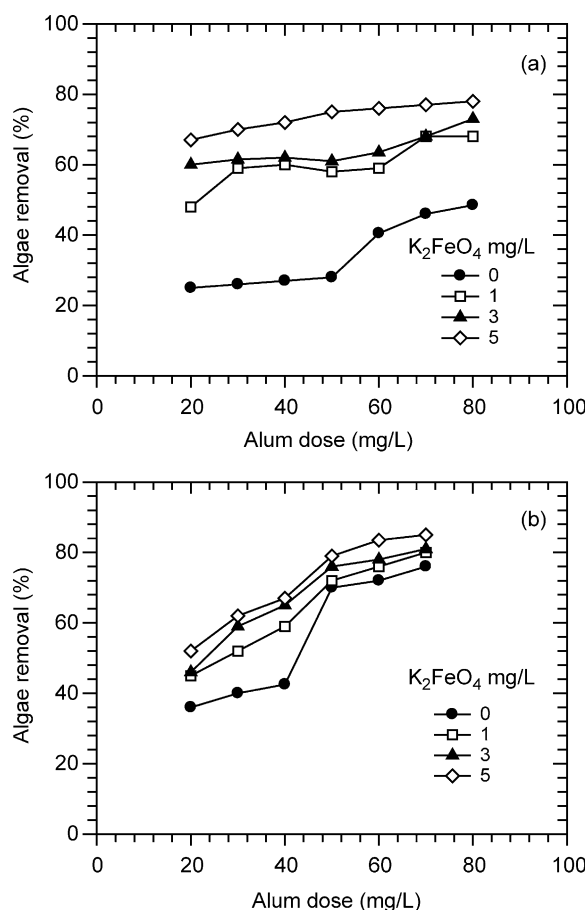


Figure 6 | Effect of Fe(VI) preoxidation on the removal of algae by coagulation. Preoxidation time: 5 min. (a) Lake water (raw water quality: turbidity 10–30 NTU; algal concentration 8×10^6 – 2×10^7 cells l^{-1} ; pH 7.5–7.7; temperature 15–18 °C). (b) Cultured solution (raw water quality: turbidity 20–40 NTU; algal concentration 3.5×10^8 – 4.2×10^8 cells l^{-1} ; pH 7.1 (adjusted); temperature 15 ± 1 °C) (reproduced from Ma & Liu 2002a).

in animals and humans through inhibition of protein phosphatases (Erickson *et al.* 1990). The microcystins are a group of monocyclic heptapeptide hepatoxins that consist of two variable L-amino acids, three D-amino acids, and two unusual amino acids. Microcystins differ mainly in the two L-amino acids, which give the molecule its name. The most common and highly toxic microcystin-LR contains leucine and arginine as variable amino acids (Figure 7). Toxicity of microcystins is related to the Adda group in the molecule. Microcystins can persist in water from days to weeks.

Many treatment methods have been investigated to remove microcystins from water. Biological methods were found to be unworkable because reaction times lasted hours

to days (Angeline *et al.* 1995). The most common chemical method, chlorination, has high dose and long contact time requirements that may result in carcinogenic by-products such as trichloromethane in water. Ozonation of water can reduce microcystins to very low levels, but the reaction is less effective at alkaline pH (Rositano *et al.* 1998). Most importantly, Fe(VI) and Fe(V) can decompose microcystins by oxidative processes very efficiently over a wide pH range.

Kinetic studies on the oxidation of microcystin amino acids by Fe(VI) and Fe(V) have been performed (Table 5). Rate constants were calculated using experimentally determined values at pH 12.4 assuming a 10-fold increase in rate per pH unit (Sharma & Bielski 1991; Bielski *et al.* 1994). The rate constants for reaction of amino acids with Fe(VI) were $\approx 10^4$ M $^{-1}$ s $^{-1}$, while the reactivity for Fe(V) is $\approx 10^5$ orders of magnitude higher than those of Fe(VI). The results in Table 5 suggest that Fe(VI) detoxifies microcystins by effectively oxidizing their amino acids (Rush & Bielski 1995). Recent experiments demonstrated extensive destruction of microcystin-LR through oxidation with Fe(VI) (Yuan *et al.* 2002). Oxidation resulted in structural destruction of a heptapeptide ring and a modification of the toxic Adda group of the microcystin-LR. The results support oxidation of amino acids by Fe(VI) in the detoxification of microcystins.

This detoxification process could be enhanced by Fe(V), which is a much more powerful oxidant than Fe(VI) (Table 5). The removal of toxins by Fe(VI) may be enhanced in the presence of appropriate one-electron reducing agents such as conduction band electrons formed in photocatalytic processes (Equation 9). A process combining ferrate and a photocatalytic would form a highly reactive Fe(V) species, which would be very effective in killing microcystins. Recent results support this contention in which detoxification efficiency of microcystins-LR was enhanced in a combination process (Xing *et al.* 2002).

Biofilm control

In aqueous environments, microbiological films are formed on surfaces, which cause detrimental effects, especially in the industrial and medical fields (Waite & Fagan 1980; Fagan & Waite 1983). In utility cooling systems, heat exchanger and pump efficiencies are reduced and in medical facilities, infections may occur. The use of chlorine to control biofilms is unsatisfactory and better alternatives

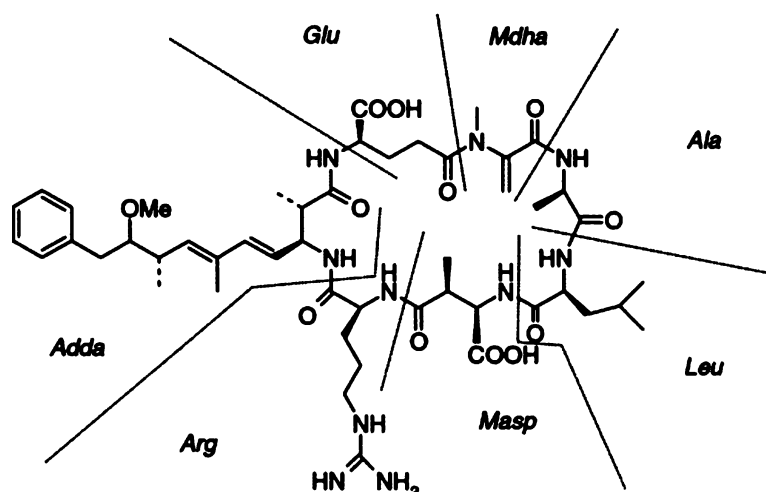


Figure 7 | Structure of the blue-green algal toxin microcystin-LR. Besides the two variable L-amino acids, leucine and arginine, the microcystin contains three D-amino acids (glutamic acid, alanine and methionine) and two unusual amino acids: *N*-methyldehydroalanine (Mdha) and 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (Adda) (reproduced from Nishiwaki *et al.* 1992).

are needed. As discussed above, Fe(VI) is a powerful biocide that can inactivate numerous microorganisms at very low concentrations and can therefore be an excellent candidate to control biofilms in water systems.

Fagan & Waite (1983) have monitored biofilm growth in model condenser systems as a function of Fe(VI) dose and contact time. Biofilm growth was retarded by periodic dosing of Fe(VI) for 5 minutes with Fe(VI) concentration of 10^{-5} M or higher (Figure 8). Results in this study also demonstrated that no repression of biofilm growth occurred at Fe(VI) concentration below 10^{-6} M. The optimum Fe(VI) dose for retarding biofilm growth was between 10^{-6} and 10^{-5} M. A similar dose of Fe(VI) is required for effective killing of bacteria in suspended systems (Fagan & Waite 1983). It is interesting to note that similar concentrations of Fe(VI) are effective for both attached systems and suspended ones.

ARSENIC REMOVAL

Arsenic contamination of groundwaters used for water resources is a global problem. Recent studies reported serious health risks due to As in drinking water. Arsenic exists in two forms, As(III) and As(V), in water. As(III) is more toxic and mobile than the As(V) species. Additionally, As(III) exists in nonionic H_3AsO_3 at pH 8, which does not adsorb efficiently to mineral surfaces (Kinniburgh & Smedley 2000). In comparison, As(V) is present as anions, H_2AsO_4^- and HAsO_4^{2-} and easily adsorbs to solid surfaces. Therefore, preoxidation of As(III) to As(V) is necessary for removal of arsenic. Because Fe(VI) acts as an oxidant and coagulant, it can be effective for remediation of arsenic from source water.

Reports have demonstrated the ability of Fe(VI) to treat water by reducing arsenic levels (Vogels & Johnson 1998; Fan *et al.* 2002; Lee *et al.* 2003a, b). The rate constant of the

Table 5 | Reaction rate constants for amino acids with Fe(VI) and Fe(V) (k , $\text{M}^{-1}\text{s}^{-1}$) at pH 10

Amino acids	Fe(VI) $\times 10^4$	Fe(V) $\times 10^9$	Amino acids	Fe(VI) $\times 10^4$	Fe(V) $\times 10^9$
Glycine	2.44	2.10	Tyrosine	37.7	2.03
Alanine	0.78	0.78	Aspartic acid	0.95	0.65
Arginine	6.32	4.97	Glutamic acid	4.27	1.21
Leucine	0.80	0.75			

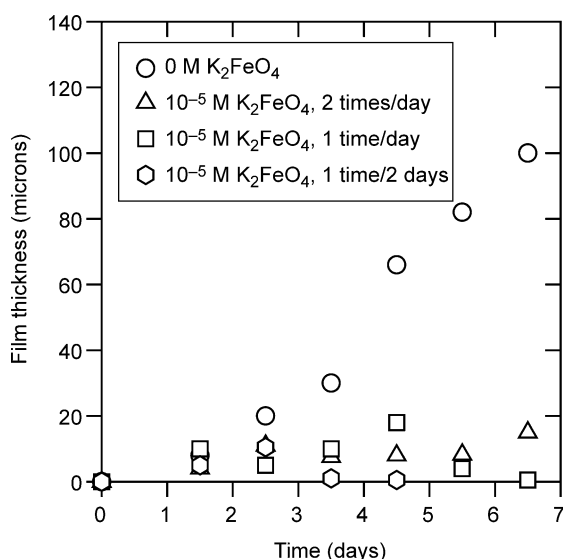
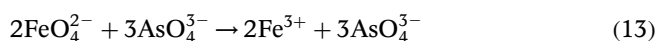
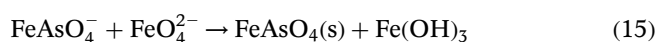


Figure 8 | Effect of Fe(VI) treatment on biofilm development (reproduced from Fagan & Waite 1983).

reaction of As(III) with Fe(VI) is determined as a function of pH (Vogel & Johnson 1998; Lee *et al.* 2003a). Rate constants suggest that As(III) is instantaneously oxidized to As(V) by Fe(VI) (Equation 13).



In the Vogel & Johnson (1998) approach, ion pairs between ferrous and As(III) were first produced before reacting with Fe(VI). An Fe(VI) reaction with this ion pair produces highly insoluble ferric arsenate, which immediately settles from solution (Equations 14 and 15).



The optimum removal of arsenic (approximately 2 ppb) was obtained with total iron/arsenate ratio $\approx 8:1$ at pH 5.0 in 50 ppb initial arsenic concentration in deionized water. The total iron is the amount of Fe(II) and Fe(VI) in solution.

Lee *et al.* (2003a, b) performed tests on river water using Fe(VI). The concentration of arsenic was lowered from 517 to below 50 ppb with addition of 2 ppm Fe(VI). Also, in this study, smaller doses of Fe(VI) (0.5 ppm) in combination with a major coagulant Fe(III) at doses 2.0 and 4.0 ppm gave similar results for arsenic removal in the river water.

These results further demonstrate the effectiveness of Fe(VI) in removing arsenic in water.

CONCLUSIONS

Fe(VI) is an effective oxidant and disinfectant for treatment of water and wastewater. Laboratory research showed that Fe(V) behaves like a radical species, which can be used to oxidize pollutants and to inactivate organisms that are difficult to treat by conventional techniques. The use of ionizing radiation and photocatalysis in the presence of Fe(VI) probably forms Fe(V) with possible synergistic effects in killing many chlorine-resistant organisms and in treating emerging toxins in aquatic environments. Thus, iron(VI) may be used to reduce levels of many chlorine-based biowarfare agents in order to ensure public health and water safety.

Pharmaceuticals, hormones and endocrine disrupting compounds have recently been recognized as emerging contaminants in source waters. Traditional treatments for water and wastewater generally do not remove these contaminants, which can then enter into surface water and groundwater sources. Ferrates' effectiveness in treating these compounds will surely be tested in future studies. Parasites, *Cryptosporidium* and *Giardia*, resist inactivation by conventional disinfectants. The potential of ferrates to treat these pathogens still needs to be determined.

Fe(VI) has been studied for many years and only now is becoming economically available in commercial quantities. In any future cost comparison between Fe(VI) and other oxidants/coagulants/disinfectants, the multi-functional properties of Fe(VI), which can be applied in a single dose should be compared with equivalent aggregate treatment costs. Additionally, in cases where Fe(VI) can effectively remove pollutants instantaneously in-line, holding tanks will not be needed in treatment facilities. The use of Fe(VI) may thus become cost effective. Fe(VI) performs coagulation at lower doses than commonly used coagulants in the water industry and this could yield less sludge production in a treatment process. The economic savings in the transportation and land application of sludge should be included in any future cost comparison calculations.

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Author Queries

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- Q1** Equations have been renumbered as we have two
Equation 12 in the manuscript