Wastewater disinfection and organic matter removal using ferrate (VI) oxidation

Erick R. Bandala, Jocelyn Miranda, Margarita Beltran, Mabel Vaca, Raymundo López and Luis G. Torres

ABSTRACT

The use of iron in a +6 valence state, (Fe (VI), as FeO_4^{-2}) was tested as a novel alternative for wastewater disinfection and decontamination. The removal of organic matter (OM) and index microorganisms present in an effluent of a wastewater plant was determined using FeO_4^{-2} without any pH adjustment. It was observed that concentrations of FeO_4^{-2} ranging between 5 and 14 mg l^{-1} inactivated up to 4-log of the index microorganisms (initial concentration c.a. 10^6 CFU/100 ml) and achieved OM removal up to almost 50%. The performance of FeO_4^{-2} was compared with OM oxidation and disinfection using hypochlorite. It was observed that hypochlorite was less effective in OM oxidation and coliform inactivation than ferrate. Results of this work suggest that FeO_4^{-2} could be an interesting oxidant able to deactivate pathogenic microorganisms in water with high OM content and readily oxidize organic matter without jeopardizing its efficiency on microorganism inactivation.

Key words | disinfection, ferrate, organic matter oxidation, wastewater, water reuse

Erick R. Bandala (corresponding author)
Departamento de Ingeniería Civil y Ambiental,
Universidad de Las Americas-Puebla,
Sta. Catarina Martir, Cholula 72820 Puebla,
Mexico
Tel.: +52 222 2292652
Fax: +52 222229200 ext. 4199
E-mail: *erick.bandala@udlap.mx*

Jocelyn Miranda
Margarita Beltran
Mabel Vaca
Raymundo López
Universidad Autónoma Metropolitana,
Unidad Azcapozalco,
Av. San Pablo 180, Mexico DF 02200,
Mexico

Luis G. Torres
Unidad Profesional Interdisciplinaria de
 Biotecnología,
Instituto Politécnico Nacional,
Av. Acueducto s/n Laguna de Ticoman,
Mexico DF 07340,
Mexico

INTRODUCTION

Lack of water is a complex problem worldwide. It has been reported that 1.2 billion people have no access to safe and affordable water for their basic needs (Rijberman 2006). Owing to this water scarcity crisis, the management of current water resources has become an important issue in several regions, mainly those with low rainfall and relatively high population density. Agriculture represents one of the most water-demanding human activities. It is well documented that, for example, producing one kilogram of cereal requires one cubic metre of water (Rijberman 2006). On average, it takes 70 times more water to grow food for people than the volume that is used directly for domestic purposes (IWMI 2004). Most of the water provided for domestic duties is returned as wastewater after its use and is able to be reused. In contrast, a considerable percentage of agricultural water (up to 90%) is evapotranspired
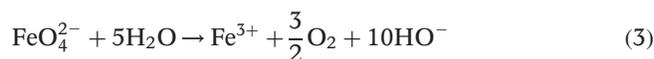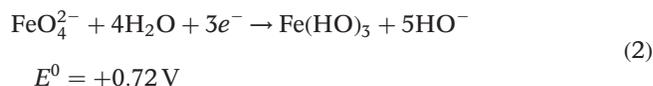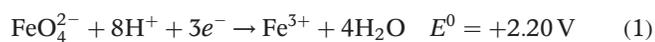
preventing further recycle. From these arguments, reduction of water withdrawn for agriculture is imperative.

Municipal wastewater reuse is an emerging approach with interesting results for agricultural water substitution. In Mexico, the area used for agriculture is about 2×10^7 ha; over 30% of this area is devoted to intensive agricultural activities involving irrigation. Agricultural wastewater reuse is a common practice; yearly, 3.4 km^3 of wastewater is used for agricultural irrigation. The use of municipal wastewater for agriculture has some advantages, such as the improvement of yields when compared with the use of surface or underground water; or the more efficient use of nutrients in the long term and the cost reduction associated with the reduced or null use of fertilizers (García *et al.* 2007).
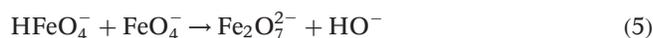
On the other hand, municipal wastewater is also a source of a wide variety of pathogenic agents able to cause

diseases as result of accidental direct ingestion of untreated or poorly treated wastewater, skin contact, and ingestion of aquatic food species or by the consumption of agricultural food products grown using untreated wastewater. In the best cases, municipal wastewater effluents are disinfected by chlorination. However, it has been well documented that many pathogenic species are resistant to chlorine-based disinfection (Corona-Vasquez et al. 2002; Orta et al. 2004; García et al. 2007). Additionally, the use of chlorine for disinfection of wastewater with a high content of organic matter is known to produce chlorinated disinfection by-products, widely documented as animal carcinogens and some of them suspected as human carcinogens (Gelover et al. 2000; Liberti et al. 2002). Alternative oxidants such as ozone, bromine and chloramines, among others, have been considered for use instead of chlorine; however they also generate by-products, many of them toxic to aquatic biota and potentially to humans (Pinagiota & Graham 2002). Another problem related to the use of these alternative disinfectants is that, as with chlorine, high organic matter concentrations interfere with the disinfection process. The use of ultraviolet (UV) radiation has been proposed as an alternative for municipal wastewater treatment to be applied in agriculture and its use has increased recently with attractive results (Liberti et al. 2002). However, the lack of residual effect in UV disinfection is probably its major inconvenience; it has been demonstrated that reactivation of bacteria is commonly observed mainly when water is disinfected with low UV doses (Zimmer et al. 2003; Otaki et al. 2003).

A novel alternative for water disinfection and decontamination included in emerging oxidation processes is the use of iron in a +6 valence state, Fe (VI), as FeO_4^{-2} (Sharma 2007; Yngard et al. 2007; Yuan et al. 2008). Ferrate (VI) is a powerful oxidant in aqueous media as suggested by their reduction potentials in reactions (1) and (2) (Sharma et al. 2005). Under acidic conditions, the redox potential (2.2 V, Jiang et al. 2007) of Fe(VI) ion is higher than those of many other oxidants used for wastewater treatment. Spontaneous reduction of FeO_4^{-2} in aqueous solutions is shown in Equation (3) (Goff & Murman 1971; Sharma et al. 2007a,b):

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \quad E^0 = +2.20\,V \qquad (1)$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(HO)_3 + 5HO^-$$
$$E^0 = +0.72\,V \qquad (2)$$

$$FeO_4^{2-} + 5H_2O \rightarrow Fe^{3+} + \frac{3}{2}O_2 + 10HO^- \qquad (3)$$

In addition to molecular oxygen, as observed from Equation (1), generation of Fe(III), considered to be innocuous in the environment, is also reported as an Fe(VI) by-product (Jiang et al. 2001, 2007; Jiang & Lloyd 2002; Read et al. 2003; Jiang 2007). The reaction rate for Equation (1) is slow at pH 9–10 and it increases at lower pH values. The actual reaction scheme for ferrate ion is proposed by Sharma et al. (1998) starting by the production of a dimmer further reduced by water to produce oxygen:

$$FeO_4^{2-} + H_2O \rightarrow HFeO_4^- + HO^- \qquad (4)$$

$$HFeO_4^- + FeO_4^- \rightarrow Fe_2O_7^{2-} + HO^- \qquad (5)$$

$$Fe_2O_7^{2-} + 2H_2O \rightarrow O_2 + H_2FeO_4^- + H_2FeO_3^- \qquad (6)$$

Ferrate (VI) oxidant is considered environmentally friendly and able to treat a wide range of contaminants (Waite 1979; Sharma 2007; Tiwari et al. 2007), including unconventional and emerging microorganisms without side reactions or by-products generation (Sharma et al. 2005). It has been evaluated for water and wastewater treatment (Sharma 2004), oxidation of cyanide (Sharma et al. 1998), phenols (Graham et al. 2004), hydrogen sulfide (Sharma et al. 1997), thiourea (Sharma et al. 1999, 2003), organic matter (Qu et al. 2003), cyanotoxins (Xing et al. 2002), surfactants (Eng et al. 2005), with satisfactory results.

Water disinfection using ferrate (VI) has been tested over the last three decades achieving disinfection at relatively low dosages for different pH values (Sharma 2004, 2007; Sharma et al. 2006; Jiang 2007). Most of these works were published at the end of the 1970s, 1980s and early 1990s, mainly focusing on surface water treatment (Murmann & Robinson 1974; Gilbert et al. 1976; Schink & Waite 1980; Kato & Kazama 1983, 1990; Kazama 1989, 1994, 1995). Despite the interesting results obtained in the application of this oxidant agent in water disinfection, relatively few works dealing with its use in the treatment of

wastewater are currently available in recent literature (Kato & Kazama 1991). The aim of this work is to test the effectiveness of FeO_4^{-2} in the removal of organic matter and pathogenic index microorganisms present in effluent of a wastewater plant focusing on its application for reuse in agricultural irrigation.

MATERIALS AND METHODS

Reagents

All chemicals used in this study were (ACS) grade reagents (Sigma-Aldrich) and were used as received without further purification. Potassium ferrate (K_2FeO_4) of high purity (97%) was prepared by the method reported by Hrostowski & Scott (1950).

Wastewater analysis

All the experiments were carried out using the effluent of a conventional wastewater treatment plant. The initial characterization of the wastewater sample was carried out for the following parameters: turbidity was measured in accordance with Mexican regulations (NOM-AA-38-1981) using a Hanna Instruments turbidimeter LP-2000; electric conductivity was determined with a YSI 85 conductimeter. Total and total dissolved solids were measured using the 2540 B and 9540 C *Standard Methods* (1992), respectively. Total and fecal coliforms were determined by the filtrating membrane method (9222 B and 9222 D *Standard Methods* 1992, respectively). Total organic carbon (TOC) was measured under the USEPA 9060 method, using a Beckman Industrial 915-B apparatus. Total residual chlorine was determined in the samples using the DPD colorimetric method (HACH DR-100).

Oxidation of organic matter

Six FeO_4^{-2} concentrations, 2, 5, 7, 9, 12 and $14 \, \mathrm{mg \, l^{-1}}$, were tested for organic matter oxidation, adding the corresponding quantity of potassium ferrate to a 500-ml effluent sample without pH adjustment. The mixture was allowed to react under continuous magnetic agitation for 10 min. After this time, the reaction mixture was filtered and the filtrate was analysed for TOC and turbidity. For comparison purposes, the organic matter oxidation was also tested using sodium hypochlorite. The hypochlorite concentrations tested and the reaction conditions were the same as those previously described for ferrate experiments. In both cases, every experiment was performed by triplicates and a blank sample (without the addition of oxidant) was carried out for every experimental set.

Water disinfection

Tests of water disinfection were carried out using, for the case of FeO_4^{-2}, the same concentrations as described above with a reaction time of 5 minutes. In the case of hypochlorite, three oxidant concentrations, 9, 12 and $14 \, \mathrm{mg \, l^{-1}}$, and twice the contact time of that reported for ferrate, were used. The sample wastewater was put in contact with the oxidant in Erlenmeyer flasks as described earlier for OM oxidation assessments. After the reaction time was completed, samples were analysed for fecal and total coliforms as described above. Disinfection tests were carried out without any pH adjustment because the actual pH value determined in the wastewater samples was in the pH range described by Jiang *et al.* (2007) as proper for disinfection tests using either FeO_4^{-2} or chlorine.

RESULTS AND DISCUSSION

Wastewater characterization

Table 1 shows the results of the initial characterization of the wastewater sample. Despite the fact that this sample was obtained from a secondary effluent, a high concentration of solids ($620 \pm 2 \, \mathrm{mg \, l^{-1}}$) as well as a considerable concentration of organic matter (measured as TOC) ranging between 80 and $110 \, \mathrm{mg \, l^{-1}}$, were observed. Total and fecal coliform concentrations were quite high, in the order of 10^6 CFU/100 ml. Since these parameters are considered as indexes of the presence of pathogenic microorganisms in the effluent, it is clear that reuse of this water for agriculture could involve important health risks for potential users. In terms of the quality of this effluent, it is evident that the secondary treatment producing this wastewater was performed unsatisfactorily. In fact, the total, suspended and

Table 1 | Results of the initial characterization of the wastewater sample used in this study

Parameter	Value range $\pm \delta$	Parameter	Value range $\pm \delta$
TOC	$80–110 \pm 3\,\mathrm{mg\,l^{-1}}$	Dissolved solids	$500 \pm 3\,\mathrm{mg\,l^{-1}}$
Turbidity	$5.10–6.39 \pm 0.06\,\mathrm{NTU}$	Suspended solids	$120 \pm 3\,\mathrm{mg\,l^{-1}}$
pH	$7.12–7.89 \pm 0.05$	Total coliforms	$12–15 \times 10^6\,\mathrm{CFU/100\,ml}$
Electric conductivity	$923–850 \pm 0.01\,\mu\mathrm{Scm^{-1}}$	Fecal coliforms	$8–13 \times 10^6\,\mathrm{CFU/100\,ml}$
Total solids	$620 \pm 2\,\mathrm{mg\,l^{-1}}$		

dissolved solids of the sample fall within the ranges that have been reported for raw municipal wastewater generated in Mexico City: for example, from the Gran Canal and the deep drainage flows, $465–925\,\mathrm{mg\,l^{-1}}$, $355–751\,\mathrm{mg\,l^{-1}}$ and $110–154\,\mathrm{mg\,l^{-1}}$, respectively, as reported by Mijaylova et al. (1996). In contrast, the total coliform concentrations reported for the Mexico City wastewaters were $0.9–3.4 \times 10^8$ CFU/100 ml, while in this work, wastewaters had a level of $8–13 \times 10^6$ CFU/100 ml.

Organic matter oxidation

The removal of organic matter (OM) content, as TOC, in the wastewater using both oxidants, FeO_4^{-2} and hypochlorite, is depicted in Figure 1. For FeO_4^{-2}, as shown, overall OM removal was directly related to oxidant concentration (correlation coefficient $R^2 = 0.995$): the higher the FeO_4^{-2} concentration, the higher the OM removal. For a FeO_4^{-2} concentration of $14\,\mathrm{mg\,l^{-1}}$, the removal of TOC concentration reached 48%; when the FeO_4^{-2} concentration was $2\,\mathrm{mg\,l^{-1}}$, a removal of only 28% was attained after one hour of reaction.

Previous work dealing with OM oxidation with ferrate (VI) have shown similar results to those obtained here. Using fulvic acid as a model for OM in drinking water, Qu et al. (2003) observed up to 87% of OM removal when a ferrate (VI) concentration of $25\,\mathrm{mg\,l^{-1}}$ was applied, for 30 minutes of reaction time. These removal results are higher than those reported in this work; nevertheless the OM concentration (as fulvic acid) used by Qu et al. (2003) was considerable lower, $2\,\mathrm{mg\,l^{-1}}$, than the $80\,\mathrm{mg\,l^{-1}}$ of TOC we have tested. Wei & Yong (2004) reported an oxidation of dissolved organic carbon (DOC) up to 19% using $5\,\mathrm{mg\,l^{-1}}$ of ferrate dosage in surface water with a high DOC concentration ($14.8\,\mathrm{mg\,l^{-1}}$). They claim that ferrate enhances the

treatment of OM-rich waters not only by chemical oxidation but also by serving as a coagulant.

The use of ferrate to enhance coagulation has also been reported mainly in surface water (Liu & Ma 2002) and even for adsorption and coagulation processes for drinking water treatment (De Luca et al. 1983). We monitored the turbidity of the wastewater after addition of ferrate in a settling flask for 20 hours in order to determine the actual potential of the process to promote coagulation besides the oxidation reaction. It was observed that the highest FeO_4^{-2} concentration ($14\,\mathrm{mg\,l^{-1}}$) was able to remove up to 88% of initial turbidity after 20 hours of settling. Wei & Yong (2004) obtained a turbidity removal of 40% using $2\,\mathrm{mg\,l^{-1}}$ of ferrate followed by $50\,\mathrm{mg\,l^{-1}}$ of alum after 30 minutes of settling. Higher or lower ferrate concentrations and alum dosages produced lower turbidity removal.

Water disinfection

The results from the application of the different FeO_4^{-2} concentrations for inactivation of fecal and total coliforms present in the wastewater effluent are presented in Table 2. As shown, except for the lowest FeO_4^{-2} concentration where
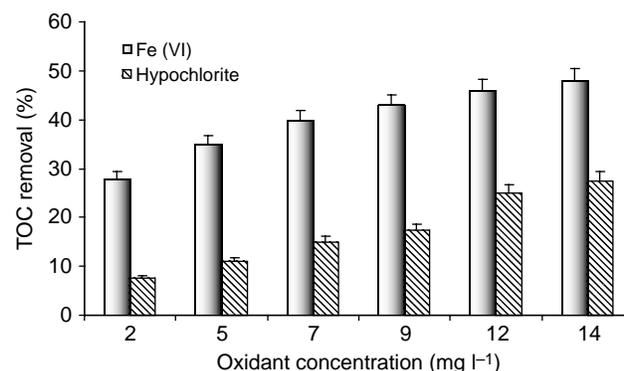
Figure 1 | Comparison between organic material (as TOC) removal due to Fe(VI), as FeO_4^{-2}, and sodium hypochlorite oxidation.

Table 2 | Results obtained from the application of the different FeO_4^{-2} concentrations to inactivation of fecal and total coliforms present in the wastewater effluent

FeO_4^{-2} doses (mg l^{-1})	Initial total coliforms, CFU/100 ml $\pm \sigma$*	Final total coliforms, CFU/100 ml $\pm \sigma^{\dagger}$	Initial fecal coliforms, CFU/100 ml $\pm \sigma$*	Final fecal coliforms, CFU/100 ml $\pm \sigma^{\dagger}$
2	9×10^6	3×10^6	4×10^6	1×10^6
5	9×10^6	ND	4×10^6	ND
9	8×10^6	ND	6×10^6	ND
12	8×10^6	ND	6×10^6	ND
14	8×10^6	ND	6×10^6	ND

*Total coliforms standard deviation ($\sigma = 5\%$).
†Fecal coliforms standard deviation ($\sigma = 10\%$).
ND, Non Detected.

a removal of 66% of total and 75% of fecal coliforms was reached, all the FeO_4^{-2} concentrations tested inactivated over 4 log of the index microorganisms in the wastewater. This is consistent with a previous report of an achievement of more than a 99.9% kill rate of total coliforms in drinking water using ferrate (Sharma *et al.* 2005). The inactivation of *Escherichia coli* using Fe(VI) has also been examined (Jiang & Wang 2003). It was determined that ferrate was capable of inactivating almost 3 log (99.9%), depending on the oxidant concentration, in 15 min of reaction time.

In Figure 2, total and fecal coliform inactivation as a function of $C \times t$ product is shown. It can be readily noted that, for FeO_4^{-2} disinfection, microorganism inactivation up to 4 log was reached for $C \times t$ values under 20 (mg l^{-1})-min, whereas when coliform inactivation was carried out using hypochlorite, it was necessary to add an oxidant concentration of 12 mg l^{-1} followed by twice the reaction time ($C \times t > 120$ (mg l^{-1})-min) to reach complete disinfection of the water. Jiang & Wang (2003) carried out a comparative study for *E. coli* inactivation using FeO_4^{-2} and hypochlorite
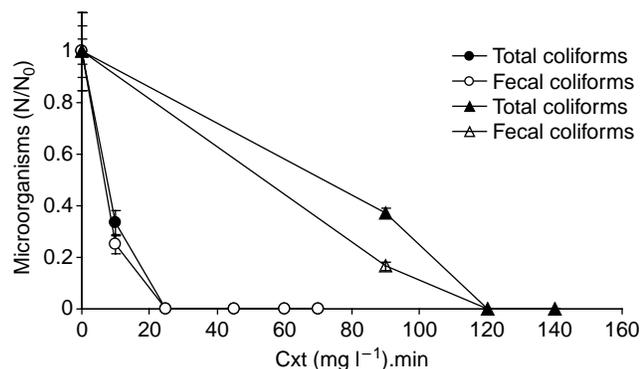
Figure 2 | Total and fecal coliform inactivation using FeO_4^{-2} (open and closed circles) and hypochlorite (open and closed triangles) as a function of $C \times t$ values.

in water, and observed that relatively higher doses and contact times were required for hypochlorite disinfection than those for FeO_4^{-2}. Overall performance of FeO_4^{-2} was superior to hypochlorite in eliminating *E. coli*. We think that this could be due to the high content of OM present in the effluent. It is well known that OM competes with microorganisms in the chlorine disinfection reaction to form disinfection by-products, decreasing the disinfection efficiency of chlorine (Kitis *et al.* 2001; Sharma *et al.* 2005). If the high TOC concentration in the effluent is considered, it seems reasonable that hypochlorite will react with OM (as we have demonstrated) before killing the bacteria, reducing its efficiency in the disinfection process. However, FeO_4^{-2} has proven to have enough potential for simultaneous oxidation of the organic matter and disinfection of the treated effluent under similar or less concentrated conditions.

It has been demonstrated that FeO_4^{-2} is a very interesting emerging alternative for water treatment; nevertheless FeO_4^{-2} preparation is complicated in the laboratory and it is very unstable under storage after preparation. Currently, our research group is focusing on the investigation of novel synthetic methodologies for FeO_4^{-2} preparation as well as the *in situ* generation of this reagent by electrochemical methods for application in environmental problems.

CONCLUSIONS

OM removal, as TOC, was directly related to the oxidant concentration: the higher the FeO_4^{-2} concentration, the higher the OM removal. For a FeO_4^{-2} concentration of 14 mg l^{-1}, TOC concentration removal reached 48%,

whereas when ferrate concentration was $2\,mg\,l^{-1}$, OM removal reached only 28% after one hour of reaction.

For FeO_4^{-2} disinfection, microorganism inactivation up to 4 log was reached for $C \times t$ values under 20 $(mg\,l^{-1})$-min, whereas when coliform inactivation was carried out using hypochlorite, it was necessary to add an oxidant concentration of $12\,mg\,l^{-1}$ and to leave twice the reaction time $(C \times t > 120\ (mg\,l^{-1}).min)$ to achieve complete disinfection of the water.

Wastewater oxidation and disinfection using FeO_4^{-2} is a promising technology, though more research is necessary.

REFERENCES

Corona-Vasquez, B., Samuelson, A., Rennecker, J. & Mariñas, B. 2002 Inactivation of *Cryptosporidium parvum* oocysts with ozone and free chlorine. *Water Res.* **36**, 4053–4063.

De Luca, S. J., Chao, A. C. & Smallwood, C. 1983 Removal of organic priority pollutants by oxidation-coagulation. *J. Environ. Eng.* **109**(1), 36–46.

Eng, Y., Sharma, V. K. & Ray, A. 2005 Ferrate (VI): green chemistry oxidant for degradation of cationic surfactants. *Chemosphere* **63**(10), 1785–1790.

García, J. L., Mejía, L., Bandala, E. R. & Corona-Vasquez, B. 2007 Helminth eggs inactivation using homogeneous photocatalysis. In *Proceedings of the VI International Congress on Environmental Sciences*, 6–8 June 2007, Chihuahua, Mexico.

Gelover, S., Bandala, E. R., Leal, M. T., Pérez, S. & Martínez, E. 2000 GC-MS determination of volatile organic compounds in drinking water supplies in Mexico. *Environ. Toxicol.* **15**, 131–139.

Gilbert, M., Waite, T. D. & Hare, C. 1976 Applications of ferrate ion to disinfection. *J. Am. Water Works Assoc.* **56**, 466–474.

Goff, H. & Murmann, R. K. 1971 Studies on the mechanism of isotopic oxygen exchange and reduction of ferrate (VI) ion (FeO_4^{2-}). *J. Am. Water Works Assoc.* **56**, 466–474.

Graham, N., Cheng, J., Xiang, L., Jia-Quian, J. & Jun, M. 2004 The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate. *Chemosphere* **56**, 949–956.

Hrostowski, H. J. & Scott, A. B. 1950 The magnetic susceptibility of potassium ferrate. *J. Chem. Phys.* **18**(1), 105–107.

IWMI 2004 Water. More nutrition per drop: Towards sustainable food production and consumption patterns in a rapidly changing world. Background report for CSD12, IWMI, New York.

Jiang, J. Q. & Wang, S. 2003 Inactivation of *Escherichia coli* with ferrate and sodium hypochlorite: a study on the disinfection performance and constant. In: A. Vogepohl (ed.) *Oxidation Technology Water Wastewater*, CUTEC-Series Publication No. 57. Papierflieger Verlag, Clausthal-Zellerfield, Germany, pp. 406–411.

Jiang, J. Q., Wang, S. & Panagoulopoulos, A. 2007 The role of potassium ferrate (VI) in the inactivation of Escherichia coli and in the reduction of COD for water remediation. *Desalination* **210**, 266–273.

Jiang, J. W. 2007 Research progress in the use of ferrate (VI) for the environmental remediation. *J. Hazard. Mater.* **146**(3), 617–623.

Jiang, J.-W. & Lloyd, B. 2002 Progress in the development and use of ferrate (VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Res.* **36**, 1397–1408.

Jiang, J. W., Lloyd, B. & Grigore, L. 2001 Preparation and evaluation of potassium ferrate as an oxidant and coagulant for potable water treatment. *Environ. Eng. Sci.* **18**(5), 323–328.

Kato, K. & Kazama, F. 1983 Biocidal studies on potassium ferrate (VI) I. The biocidal effects relating to the nature of water samples from urban river and sewage plant. *Water Purif. Liquid Waste Treat.* **24**, 929–934.

Kato, K. & Kazama, F. 1990 Respiratory inhibition of Sphaerotilus by iron compounds and the distribution of the sorbed iron. *Water Sci. Technol.* **23**, 947–954.

Kato, K. & Kazama, F. 1991 Biocidal characteristics of potassium ferrate. In *Proceedings of the 3rd IAWPRC Regional Conference on Asian Water Quality*, 20–24 November 1991, Shanghai, China.

Kazama, F. 1989 Respiratory inhibition of Sphaerotilus by potassium ferrate. *J. Ferment. Bioeng.* **67**, 369–373.

Kazama, F. 1994 Inactivation of coliphage Qß by potassium ferrate. *FEMS Microbiol. Lett.* **118**, 345–350.

Kazama, F. 1995 Viral inactivation by potassium ferrate. *Water Sci. Technol.* **31**, 165–168.

Kitis, M., Karanfil, T., Kilduff, J. E. & Wigton, A. 2001 The reactivity of natural organic matter to disinfection by-products formation and its relation to specific ultraviolet absorbance. *Water Sci. Technol.* **43**(2), 9–16.

Liberti, L., Notarnicola, M. & Petruzzeli, D. 2002 Advanced treatment for municipal wastewater reuse in agriculture. UV disinfection: parasite removal and by-product formation. *Desalination* **152**, 315–324.

Liu, W. & Ma, J. 2002 Effects of ferrate (VI) preoxidation on the architecture of algae cells and the mechanism of enhanced coagulation. *Acta Sci. Circumst.* **22**(1), 24–28.

Mijaylova, P., Torres, L. G., Ramirez, E., Lopez, S. & Cardoso, L. 1996 Characterization and coagulation. Flocculation treatability of Mexico City wastewater applying ferric chloride and polymers. *Water Sci. Technol.* **34**(3–4), 235–247.

Murmann, R. H. & Robinson, P. R. 1974 Experiments utilizing FeO_4^{2-} for purifying water. *Water Res.* **8**, 543–547.

Orta, M. T., Martínez, J. L., Monje, I. & Rojas, M. N. 2004 Destruction of helminth (*Ascaris suum*) eggs by ozone. *Ozone Sci. Eng.* **26**, 359–366.

Otaki, M., Okuda, A., Tajima, K., Iwasaki, T., Kinishita, S. & Ohgaki, S. 2003 Inactivation differences of microorganisms by low pressure UV and pulsed xenon lamps. *Water Sci. Technol.* **47**, 185–190.

Pinagiota, P. & Graham, J. D. 2002 Ozonation of municipal wastewater effluents. *Water Environ. Res.* **74**, 569–581.

Qu, J., Liu, H. Q., Liu, S. & Lei, P. J. 2003 Reduction of fulvic acid in water by ferrate. *J. Environ. Eng.* **129**(1), 17–24.

Read, J. F., Graves, C. R. & Jackson, E. 2003 The kinetics and mechanism of the oxidation of the thiols 3-mercapto-1-propane sulfonic acid and 2-mercaptonicotinic acid by potassium ferrate. *Inorg. Chim. Acta* **384**, 41–49.

Rijberman, F. R. 2006 Water scarcity: fact or fiction? *Agric. Water Manage.* **80**(1–3), 5–22.

Schink, T. & Waite, T. D. 1980 Inactivation of f2 virus with ferrate (VI). *Water Res.* **14**, 1705–1717.

Sharma, V. K. 2004 Use of iron (VI) and iron (V) in water and wastewater treatment. *Water Sci. Technol.* **49**(4), 69–74.

Sharma, V. K. 2007 Disinfection performance of Fe(VI) in water and wastewater: a review. *Water Sci. Technol.* **55**(1), 225–232.

Sharma, V. K., Smith, J. & Millero, F. 1997 Ferrate (VI) oxidation of hydrogen sulfide. *Environ. Sci. Technol.* **31**, 2486–2491.

Sharma, V. K., Rivera, W., Smith, J. & O'Brien, B. 1998 Ferrate (VI) oxidation of aqueous cyanide. *Environ. Sci. Technol.* **32**, 2608–2613.

Sharma, V. K., Rivera, W., Vishwas, N. J., Millero, F. & O'Connor, D. 1999 Ferrate (VI) oxidation of thiourea. *Environ. Sci. Technol.* **33**, 2645–2650.

Sharma, V. K., Winkelmann, K., Krasnova, Y., Lee, Ch. & Sohn, M. 2003 Heterogeneous photocatalytic reduction of ferrate VI in UV-irradiated suspensions: role in enhancing destruction of nitrogen-containing pollutants. *Int. J. Photoenergy* **5**(3), 183–190.

Sharma, V. K., Kazama, F., Jiangyong, H. & Ray, A. 2005 Ferrates (iron VI and iron (V)): environmentally friendly oxidants and disinfectants. *J. Water Health* **3**(1), 45–58.

Sharma, V. K., Mishra, S. K. & Nesnas, N. 2006 Oxidation of sulfonamide antimicrobials by ferrate (VI) (Fe $^{VI}O_4^{2-}$)$^+$. *Environ. Sci. Technol.* **40**, 7222–7227.

Sharma, V. K., Yngar, R. A., Cabelli, D. E. & Baum, J. C. 2007a Ferrate (VI) and ferrate (V) oxidation of cyanide, thiocyanate and copper (I) cyanide. *Rad. Phys. Chem.* **77**(6), 761–767.

Sharma, V. K., Dutta, P. K. & Ray, A. K. 2007b Review of kinetics of chemical and photocatalytical oxidation of arsenic (III) as influenced by pH. *J. Environ. Sci. Health A* **42**(7), 997–1004.

Standard Methods for the Examination of Water and Wastewater 1992 18th edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Tiwari, D., Kim, H., Choi, B., Lee, S., Kwon, O., Choi, K. & Yang, J. 2007 Ferrate (VI): a green chemical for the oxidation of cyanide on aqueous/waste solids. *J. Environ. Sci. Health A* **42**(6), 803–810.

Waite, T. D. 1979 Feasibility of wastewater treatment with ferrate. *J. Environ. Eng.–ASCE* **105**, 1023–1026.

Wei, L. & Yong, L. 2004 Use of ferrate pre-oxidation in enhancing the treatment of NOM-rich lake waters. *Water Sci. Technol. Water Supply* **4**(4), 121–128.

Xing, H., Yuan, B., Wang, Y. & Qu, J. 2002 Photocatalytic detoxification of microcystins combined with ferrate pretreatment. *J. Environ. Sci. Health A* **37**(4), 641–649.

Yngard, R., Damrongsiri, S., Osathaphan, K. & Sharma, V. K. 2007 Ferrate (VI) oxidation of zinc-cyanide complex. *Chemosphere* **69**(5), 729–735.

Yuan, B. L., Li, X. & Graham, N. 2008 Aqueous oxidation of dimethyl phthalate in a Fe(VI)-TiO$_2$-UV reaction system. *Water Res.* **42**(6–7), 1413–1420.

Zimmer, J. L., Slawson, R. M. & Huck, P. M. 2003 Inactivation and potential repair of Cryptosporidium parvum following low medium-pressure ultraviolet irradiation. *Water Res.* **37**, 3517–3523.