Ferrate(VI) Oxidation of Endocrine Disruptors and Antimicrobials in Water

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ASTRACT

Potassium ferrate(VI) (K_2FeO_4) has advantageous properties such as a dual function as an oxidant and disinfectant with a non-toxic byproduct, iron(III), which makes it an environmentally friendly chemical for water treatment. This paper presents an assessment of the potential of ferrate(VI) to oxidize representative endocrine disruptors (EDs) and antimicrobials during water treatment using information about reaction kinetics and products. Selected EDs were bisphenol A (BPA) and 17α-ethynylestradiol (EE2), estrone (E1), 17*β*-estradiol (E2), and estriol (E3), and sulfonamides and tetracycline were representative pharamaceuticals. The second-order rate constants, *k*, of the oxidation reactions at neutral pH were in the range from 6.50 –11.8 x 10^2 $M^{-1}s^{-1}$ and 0.79 – 15.0x10^2 $M^{-1}s^{-1}$ for EDs and sulfonamides, respectively. At a 10 mg/L K_2FeO_4 dose, half-lives of the oxidation reaction would be in seconds at a neutral pH. The values of *k*, and the reaction half-lives, varied with pH. Oxidation products from the reaction with BPA and sulamethoxazole (SMX) at molar ratios of ~ 5:1 were found to be relatively less toxic. Overall, ferrate(VI) oxidation could be an effective treatment method for the purification of waters containing these particular EDs and antimicrobials.

Keywords: Ferrate; Bisphenol; Estrogens; Sulfamethoxazole; Tetracycline; Removal

INTRODUCTION

Endocrine disruptors (EDs) are compounds that mimic natural hormones in the endocrine system thus cause adverse effects on human and wildlife (Lutz & Kloas 1999). Examples of EDs include natural steroids hormones, synthetic hormones, alkylephenols, bisphenol-A, and phthalate plasticizers. In recent years, several studies have found a variety of EDs in surface waters (Snyder et al. 2003; Westerhoff et al. 2006). In addition to EDs, pharmaceuticals and personal care products (PPCPs) have also been found in the aquatic environment (Ternes et al. 2004; Khetan & Collins 2007). Although levels of pharmaceuticals have been determined in the concentration range of ng/L to- µg/L, mixtures of pharmaceuticals even at ng/L can inhibit cell proliferation (Gibson et al. 2005; Pomati et al. 2006). EDs and PPCPs may thus affect the ecology of the environment (Jobling et al. 1998; Mills & Chichester 2005). For example, some EDs have demonstrated mutagenic and carcinogenic effects (Khetan & Collins 2007). Of the several compounds of PPCPs, detection of antibiotics is of concern due to the possibility of increased bacterial resistance (Gould 1999).

In general, drinking water utilities abstract water from various sources such as, ground water, rivers, streams, springs, or lakes in a watershed; small communities generally receive water from aquifers, while large metropolitan areas receive water from surface sources. In most cases source waters require treatment before use in order to meet national quality standards. Human populations may possibly be exposed to EDs and antibiotics through drinking water produced from surface and ground waters contaminated with such compounds in wastewater discharges and urban runoff (Weyer & Riley 2001; Snyder et al. 2003; Ongerth & Khan 2003). Importantly, the existence of such compounds in treated water indicates that plant treatment processes do not adequately remove these compounds (Ternes et al. 2002; Carbala et al. 2004;

Miao et al. 2004). Among the oxidation processes applied in water treatment, chlorine is commonly used as a pre-oxidant and disinfectant. Although chlorine is effective in oxidizing EDs and antibiotics (Deborde et al. 2004; Dodd et al. 2004; Lee et al. 2004; Pinkson et al. 2004; Dodd & Hunag 2007), oxidation reactions produce biologically active by-products (Hu et al. 2002, 2003). Those who favour the use of chlorine usually cite its ability to react with ammonia and organic nitrogen to produce chloroamines (Pinkson et al. 2004), which help to reduce trihalomethanes. However, the reactivity of chloroamines with compounds is much slower than that of free chlorine ($HOCl/OCl^-$), and there are growing concerns about the formation of nitrosomines and other nitrogen-containing byproducts in chloraminated waters.

Alternatively, ozone can be applied, which can effectively oxidize EDs and antibiotics (Huber et al. 2003, 2005; Ning et al. 2007), however, due to the potential formation of the bromate ion and other organic by-products, ozonation is not always suitable. Chlorine dioxide (ClO_2) is another oxidant used for disinfection, but its use is restricted to high quality water such as treated surface water (Gates 1998). Dosing of ClO_2 must be kept low, for example, in the United States, dosages ranging from 1.0 to 1.4 mgL^{-1} are used mainly for the preoxidation of surface water (Gates 1998). Reduction of ClO_2 produces chlorite ion, which is considered a blood poison (Condies 1986) and higher dosages of ClO_2 (>1.4 mgL^{-1}) are likely to produce chlorite levels that exceed the USEPA standard of 1 mgL^{-1}.

Ferrate(VI) ($Fe^{VI}O_4^{2-}$) is an emerging water-treatment chemical, which can address the concerns raised by the currently used oxidants (Sharma 2007a). Interestingly, ferrate(VI) does not react with bromide ion; carcinogenic bromate ion would thus not be produced in the treatment of bromide-containing water (Sharma 2006b). Additionally, ferrate(VI) exhibits many advantageous properties, including a higher reactivity and selectivity than traditional oxidant

alternatives, and a significant capability as a disinfectant, antifoulant, and coagulant (Jiang & Lloyd 2002; Sharma 2002; Sharma et al. 2005a). The spontaneous decomposition of ferrate(VI) in water forms molecular oxygen (eq 1).

$$2\ FeO_4^{2-} + 5\ H_2O \rightarrow 2\ Fe^{3+} + 3/2\ O_2 + 10\ OH^- \quad (1)$$

Moreover, the by-product of ferrate(VI) is a non-toxic ferric ion, Fe(III). This fact makes ferrate(VI) an "environmentally friendly" oxidant. Additionally, the ferric oxide produced from ferrate(VI) acts as an effective coagulant that is suitable for the removal of metals, non-metals, radionuclides, and humic acids (Sharma 2002, Sharma et al. 2005b).

This paper describes the potential of ferrate(VI) to oxidize representative EDs and antibiotics during water and wastewater treatment. Reaction kinetics information for the oxidation of bisphenol (BPA), steroid estrogens, and antibiotics by ferrate(VI) is provided to determine nominal half-lives of the oxidation processes. The current knowledge of the nature of products from the oxidation is summarized.

ENDOCRINE DISRUPTORS

BPA and Estrogens

Among the prominent EDs of environmental significance, two synthetic endocrine disrupting chemicals, bisphenol A (BPA) and 17α-ethynylestradiol (EE2), and three natural EDCs, estrone (E1), 17β-estradiol (E2), and estriol (E3) were chosen to investigate and quantify their reaction kinetics with ferrate(VI) (Li et al. 2005, 2007); all five have a common character in that they are phenolic-type compounds. Details of the experiments have been reported elsewhere (Li et al. 2005, 2007) and which involved the use of high purity potassium ferrate prepared by a method based on the oxidation of ferric nitrate with hypochlorite (Li et al. 2005). The reactions were

shown to follow an overall second-order kinetic model and the rate constants at pH 7.0 and 8.0 at 25 ^{o}C are given in **Table 1**. The rates at the two pH values were calculated from the individual rates for the reactions of ferrate(VI) species (monoprotonated, $HFeO_4^-$ and un-protonated, FeO_4^{2-}) with un-dissociated (ED) and dissociated (ED^-) endocrine disruptor species. The rate constants for the oxidation of BPA and EE2 by ferrate(VI) at pH 8.0 were found to be lower than that at pH 7.0 (**Table 1**); this was also observed by Lee et al (2005). Interestingly, no significant differences in rate constants for the oxidation of the estrogens E1, E2, and E3 were observed (**Table 1**) and therefore removal of these estrogens by ferrate(VI) can be carried out at either pH 8.0 or 7.0 without any difference in the effectiveness of the process. The greater degradation performance of BPA and EE2 by ferrate(VI) at the lower pH may be related to the higher oxidizing power of $HFeO_4^-$ than that of FeO_4^{2-} and that the fraction of $HFeO_4^-$ increases with decreasing pH. Overall, the extent of the ferrate(VI) oxidation will vary with the aqueous conditions since pH, in particular, affects the nature of the ferrate(VI) ion (degree of protonation) and the extent of dissociation of the EDs.

Generally, the application of potassium ferrate(VI) can achieve a major removal of selected EDs within seconds (**Table 1**). The reaction of BPA with ferrate(VI) was studied in detail in order to identify the formation of intermediate reaction products and the BPA degradation pathways. From the analyses carried out by LC/MS-MS and GC/MS-MS, nine specific compounds were identified, including *p*-isopropylphenol, *p*-isopropenylphenol, *4*-isopropanolphenol, and dicarboxylic acids (eg. oxalic acid). Whilst under some conditions (e.g. ferrate:BPA molar ratio ~ 5:1) BPA can be completely degraded in less than 5 minutes, the degree of organic mineralization was significantly less than 100%, indicating the presence of reaction products which persist well beyond the disappearance of the BPA (Li et al. 2007). A

pathway of BPA degradation with ferrate(VI) has been proposed as described by *Scheme I*.

ANTIMICROBIALS

Sulfonamides

The rate-law for the oxidation of sulfonamide (S) by ferrate(VI) were found to be first-order for each reactant and can be written as:

$$-d[Fe(VI)]/dt = k[Fe(VI)]_{tot}[S]_{tot} \quad (2)$$

where *k* represents the second-order rate constant for the reaction of ferrate(VI) with sulfonamide, $[Fe(VI)]_{tot}$ represents the total concentration of Fe(VI) species, and $[S]_{tot}$ represents the total concentration of each sulfonamide species. The observed second-order rate constants decreased non-linearly with increasing pH (Sharma et al. 2006). The values of *k* at pH 7.0 and 8.0 at 25 ^{o}C are reported in Table 1. If there is excess Fe(VI) concentration (10 mgL^{-1} K_2FeO_4) relative to the sulfonamides in water, as might be expected in practice, the half-lives of the reactions would be short and in the range from 39.3 to 365 s at pH 8.0 (**Table 1**). The reaction rates are pH dependent, thus, so are the half-lives of the reactions (**Table 1**). At pH 7.0 under the same conditions, the half-lives would be very short from 9.2 – 33.9 s (**Table 1**). It should also be pointed out that reaction rates are also temperature dependent, gaving rise to different activation energies of the reaction (Sharma et al. 2006). Therefore, the reaction half-lives will vary significantly with the aqeous environmental conditions.

The oxidation of sulfamethoxazole (SMX) by ferrate(VI) has been found to follow a molar stoichiometry of 4:1 ([Fe(VI):[SMX]). An evolution of one mole of oxygen per mole of SMX was determined (eq 3).

$$4\ HFeO_4^- + SMX \rightarrow 4\ Fe(III) + O_2 + Product(s) \quad (3)$$

For product analysis of the reaction, 0.750 L of 2.0x 10^{-4} M SMX was oxidized with 0.750 L of 0.001 M Fe(VI) at a pH of 9.0 for 3 hours. The reaction mixture was frozen and lyophilized using a Freeze Dry System/Freezone 4.5 (Labconco); followed by extraction procedures (Sharma et al. 2006). Products of the reaction were determined using thin-layer chromatography (TLC), column chromatography, infrared (IR) spectroscopy, ^{1}H nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry (ESI MS) techniques. Three products A, B, and C were determined as given in *Scheme II*.

Interestingly, the reaction resulted in the oxidation of either the isoxazole moiety or the aniline unit of SMX by ferrate(VI). Thus, product A indicates opening of the isoxazole moiety while the presence of predominantly a nitroso and a nitro group in product C and B, respectively, indicates ferrate(VI) attack at the aniline unit. It is possible that at higher molar ratios of ferrate(VI) to SMX, simultaneous oxidation of both the isoxazole and the aniline units might occur. It is possible that such products carry increased polarity and might have been retained on the column during chromatography. Therefore the three products described in Scheme 1 may not necessarily represent all the products of ferrate(VI) oxidation, but rather the ones that were isolated and characterized. Importantly, the oxidation of the compound by ferrate(VI), whether by the attack on the aromatic or isoxazole rings, will undoubtedly cause the oxidized product to have a differing biological binding property. It is expected that an oxidation of the amino group and/or an oxidation of the isoxazole ring (which leads to its potential opening/destruction) will change its binding properties sufficiently rendering it less of a mimic for the important *p*-aminobenzoic acid. The latter is necessary in the synthesis of the essential vitamin: folic acid. Thus ferrate(VI) not only removes SMX in water, but also produces by-products that are expected to be less toxic.

Tetracyacline

The oxidation of tetracycline by ferrate(VI) has been conducted and a stoichiometry of 1.4:1 (Fe(VI):tetracycline) was proposed (eq 4) (Yang & Doong 2006).

$$1.4\ FeO_4^{2-} + \text{tetracycline} \rightarrow 1.4\ Fe(III) + O_2 + \text{product(s)} \quad (4)$$

The effect of pH on the degradation of tetracycline showed that the removal efficiency of tetracycline increased with increase in pH (**Figure 1**). The efficiency was only 35% at pH 7.5, but increased to 53-64% when the pH of solutions were higher than 8.3. The results clearly demonstrate that pH is a critical parameter in controlling the degradation of tetracycline by ferrate(VI).

The degradation of tetracycline by ferrate(VI) was also examined by the electrospray ionization-mass spectrometry (ESI-MS) technique (Yang & Doong 2007). In an experiment 200 μM tetracycline was mixed with 50 μM ferrate(VI) and the spectral analysis of tetracycline before and after the reaction was carried out. An expected abundant peak at *m/z* 410.0 and a small peak at m/z 427 appeared for tetracycline before mixing with ferrate(VI) (Cherlet et al. 2003*)*. After the reaction, a substantial decrease in peaks at m/z 445 and 410 was observed, clearly showing the degradation of tetracycline by ferrate(VI). Additionally, total organic carbon (TOC) analysis also showed that the TOC decreased from an initial concentration of 17.65 mg-C/L to 15.65 mg-C/L after the reaction. However, it is difficult to identify the possible products from the ESI-MS spectra and TOC analysis from the results obtained in this study. Further experiments are necessary to clarify the mechanisms and reactive pathways of tetracycline by ferrate(VI).

CONCLUSIONS

Although ferrate(VI) has shown promise to be capable of oxidizing organic micro-pollutants at low levels, the reactions of ferrate(VI) with a wide range of EDs and PCCPs have yet to be investigated to fully assess the potential of ferrate(VI) to degrade these compounds. The kinetic data on pharmaceuticals are only limited to sulfonamides and ibuprofen; hence, it is important to include other drug molecules. Moreover, the nature of the products formed during the oxidation of EDs and pharmaceuticals by ferrate(VI) remains relatively unknown. Because the products can be toxic during transformation of such compounds, it is imperative to perform product studies on the oxidation by ferrate(VI). Finally, it is important to note that the application of ferrate(VI) offers the additional treatment mechanism of coagulation/solid phase adsorption via its reduced Fe(III) species, and thus future studies need to evaluate the overall effect of oxidation and coagulation/adsorption on the removal of the parent compounds and daughter products.

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Table 1. Second-order rate constants for selected EDs and antibiotics in reaction with ferrate(VI) (pH 7.0 and 8.0; 25 ^{o}C).

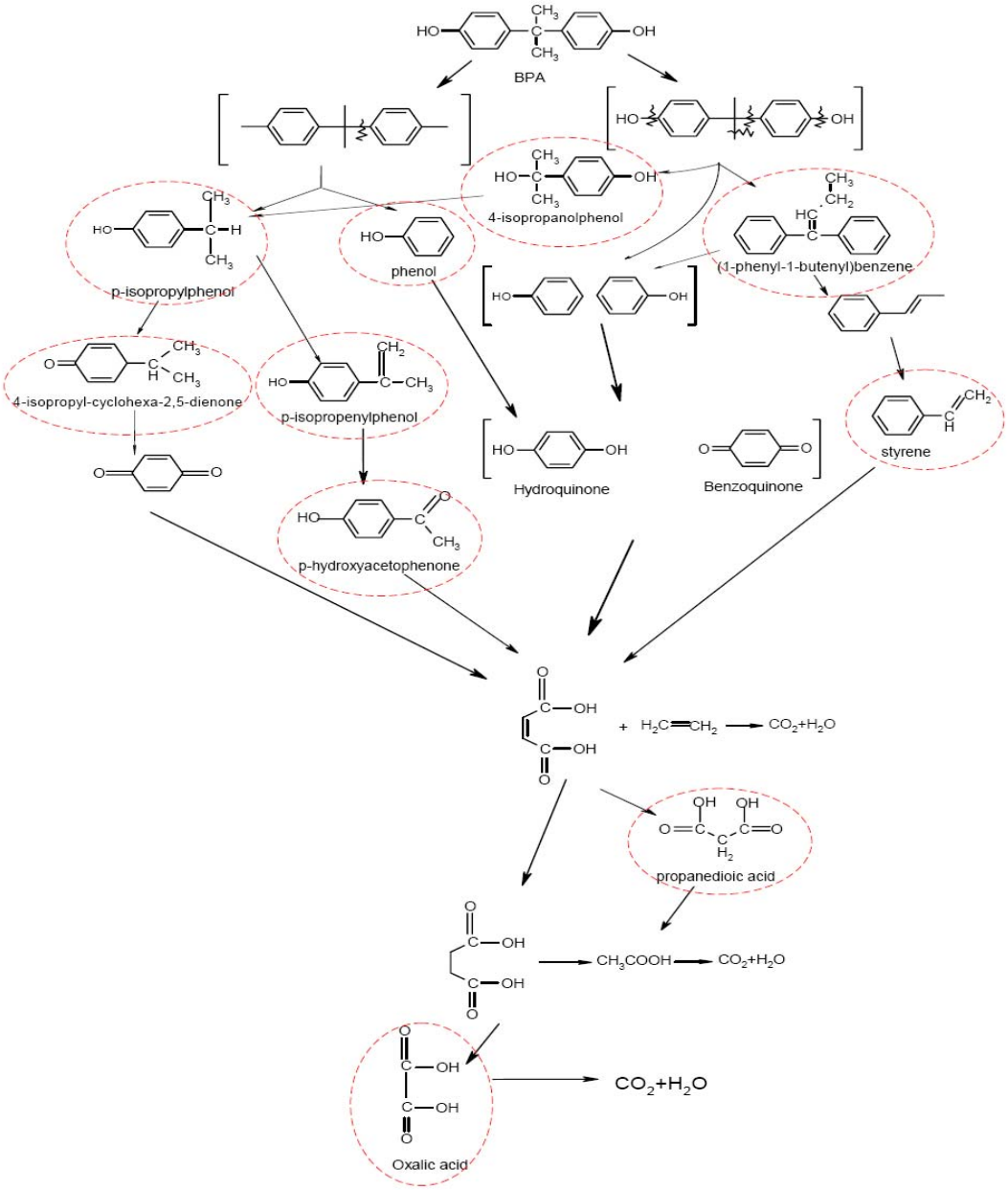
Compound	k ($M^{-1}s^{-1}$) pH 8.0	$t_{1/2}$*	k ($M^{-1}s^{-1}$) pH 7.0	$t_{1/2}$*
		EDCs[1]		
Bisphenol A (BPA)	$4.29x10^2$	32.3 s	$6.50x10^2$	21.2 s
17α-ethynylestradiol (EE2)	$6.88x10^2$	21.1 s	$8.13x10^2$	17.0 s
Estrone (E1)	$1.05x10^3$	13.1 s	$1.01x10^3$	13.7 s
B-estradiol (E2)	$1.09x10^3$	12.6 s	$1.09x10^3$	12.6 s
Estriol (E3)	$1.29x10^3$	11.6 s	$1.18x10^3$	10.9 s
		Antimicrobials[2]		
Sulfisoxazole	$3.52\pm0.10x10^2$	39.3 s	$1.50\pm0.03x10^3$	9.2 s
Sulfamethazine	$1.11\pm0.02x10^2$	125 s	$1.05\pm0.08x10^3$	13.2 s
Sulfamethizole	$0.38\pm0.01x10^2$	365 s	$4.09\pm0.41x10^2$	33.9 s
Sulfadimethoxine	-	-	$0.79\pm0.07x10^2$	175 s
Sulfamethoxazole	$0.46\pm0.02x10^2$	301 s	$1.33\pm0.08x10^3$	10.4 s

*assuming 10 mg/L K_2FeO_4 dose

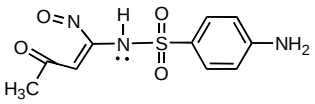
[1] The rate constants calculated using the values and kinetic equation (12) given in Li et al (2007)

[2]Sharma et al (2006)

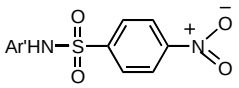
Scheme I


BPA
4-isopropanolphenol
p-isopropylphenol
phenol
(1-phenyl-1-butenyl)benzene
4-isopropyl-cyclohexa-2,5-dienone
p-isopropenylphenol
styrene
Hydroquinone
Benzoquinone
p-hydroxyacetophenone
propanedioic acid
Oxalic acid
CO2+H2O

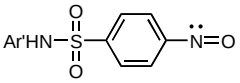
Scheme II



Product A

4 $HFeO_4^-$ + SMX → 

Product B



Product C

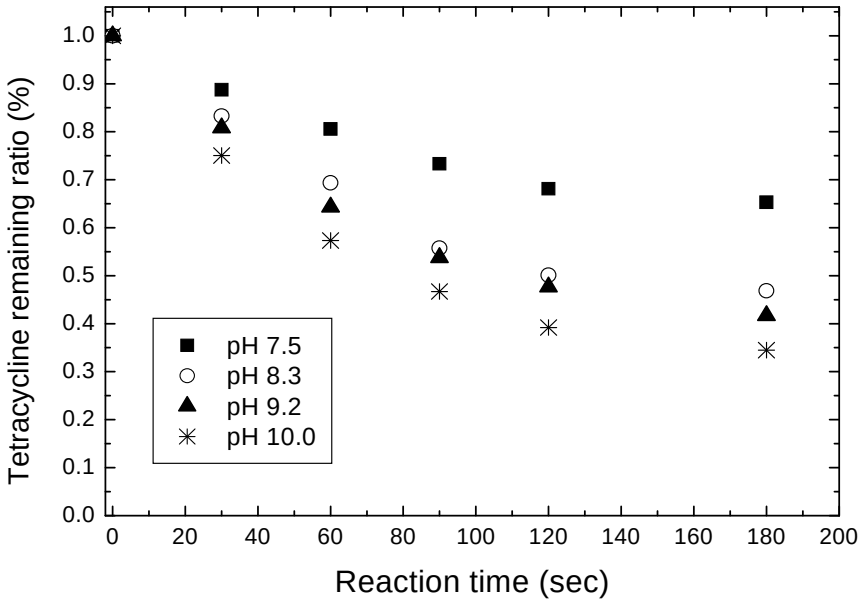


Figure 1. Degradation of tetracycline by ferrate(VI) at different pH. Experimental conditions: [Ferrate(VI)] = 50 μM; [Tetracycline] = 200 μM (adapted from Yang & Doong 2007).