REMOVAL OF EMERGING MICRO POLLUTANTS BY FERRATE(VI)

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ABSTRACT

Ferrate (VI) exhibits many advantages because of its dual functions of oxidation and coagulation. Removal of micro pollutants by ferrate(VI) was pH dependant and this was in coordinate to the chemical/physical properties of the pollutants and ferrate(VI) speciation. Promising performance of ferrate(VI) in the treatment of real waste water was observed. It is important to determine whether the ferrate(VI) treated water contains any toxic or mutagenic substances as this should relieve public health concerns when a new chemical is employed for water treatment. The toxicity studies on the ferrate(VI) treated effluent were carried out initially via Ames tests and recently via zebrafish embryos tests conducted at author’s group. These results suggest that ferrate(VI) reagents do not produce mutagenic by-products for study conditions. However, a recent other study showed the formation of adsorbable organic haloids (AOX) as by-products in the ferrate(VI) treated waste water effluents. Obviously, more researches are needed to investigate the formation potential of harmful by-products during ferrate(VI) treatment.

Keywords Emerging micro pollutants; ferrate(VI); oxidation; toxicity study; waste water treatment

1. INTRODUCTION

Pharmaceutical and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) are classified as emerging micro-pollutants because they may be significant adverse environmental effects although these pollutants in the environment are under a very low concentration range; from several µg L\(^{-1}\) to ng L\(^{-1}\). Pharmaceuticals such as antibiotics, anti-inflammatory drugs, β-blockers and X-ray contrast media are widely used, these pharmaceuticals and their metabolites are inevitably emitted into the waters by excretion (e.g., Lishman et al., 2006; Comeau et al., 2008) and/or through the discharge of industry effluents and hospitals waste waters (Ternes, 1998; Lee et al., 2007).

Endocrine disrupting chemicals (EDCs) are defined as the natural and/or synthetic compounds which would affect endocrine systems of fishes and other aqueous animals. Since the middle of last decade, a variety of adverse effects of EDCs on the endocrine systems of animals have been observed (Piva & Martini, 1998; Thorpe et al., 2001). These effects may be cumulative, possibly will only appear in subsequent generations, and then the resulting effects may be irreversible, threatening the human’s sustainable development. Most EDCs are synthetic organic chemicals being introduced to the environment by anthropogenic inputs, (e.g., bisphenol A) but they can also be naturally generated estrogenic hormones, e.g., estrone (E1) and 17β-estradiol (E2), and therefore are ubiquitous in aquatic environments receiving wastewater effluents.

Personal care products (PCPs) represent a large group of compounds which include non-prescription and prescription pharmaceuticals for human and veterinary use, and the active and inert ingredients for personal care purposes. Most PCPs, in their original or biologically altered form, are discharged into wastewater and make their way to wastewater treatment plants. Possible fates of PCPs and their metabolites within a
wastewater treatment plants are: 1) mineralization to CO$_2$ and water; 2) retention to the solids portion (sludge/biosolids) if the compound entering the plant or the product of biologically mediated transformation is lipophilic; 3) release to the receiving water either as the original compound or as a degradation product.

The presence of emerging micro pollutants and their potential toxicity are challenge to water industries as there is no unit process specifically designed to remove these pollutants; activated sludge and secondary sedimentation in most wastewater treatment works (WWTWs) seems to be inefficient to eliminate them (e.g., Castiglioni et al., 2006; Santos et al., 2007). Thus, a number of recent studies have been carried out to explore suitable technologies to treat micro pollutants residuals from water and wastewater. Ozonation (Okuda et al., 2008) and activated carbon adsorption (Snyder et al., 2007) were found to be effective to remove micro pollutants in municipal WWTWs. Nanofiltration (NF) and reverse osmosis (RO) membrane filtration have been applied at bench, pilot and full scale (Comerton et al., 2007). This paper aims to present recent studies from various research groups on the use of ferrate(VI) to treat micro pollutants and suggest research needs in this area.

2. FERRATE(VI) AND ITS APPLICATION IN WATER AND WASTEWATER TREATMENT AND IN DEGRADATION OF EMERGING MICRO POLLUTANTS

A promising technique which can address the concerns on emerging micro pollutants is ferrate (VI) which exhibits many advantages because of its dual functions for the oxidation and coagulation and it has green chemical properties (Jiang et al., 2001, 2002, 2006, 2007; Jiang, 2007; Sharma, 2002). Ferrate(VI) has been successfully applied into water remediation processes (Jiang et al., 2009; 2012; Stanford et al., 2010; Sharma, 2010; Sharma et al., 2012). The removal of pharmaceuticals and other micro pollutants by ferrate(VI) have been extensively studied (e.g., Jiang et al., 2005, 2012, 2013; Jiang and Zhou, 2012, 2013; Sharma et al., 2008).

2.1. General water and waste water treatment by ferrate(VI)

Ferrate(VI) can act as coagulant, disinfectant and oxidant. An early study conducted by the author (Jiang et al., 2001) demonstrated in comparison with ferric sulfate (FS), ferrate(VI) can achieve high organic matter removal as DOC (Figure 1).

In a study (Stanford et al., 2010) using ferrate(VI) for raw sewage treatment, much smaller dose of ferrate(VI) was required, in comparison with ferric sulfate (FS, Fe$^{3+}$), to efficiently remove suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD) and phosphorous (P).

Ferrate(VI) is efficient in inactivating *Eschericha coli*, total coliforms and f2 coliphage viruses (Kazama 1995). Figure 2 shows significant fast rates of E. coli inactivation by ferrate(VI) with smaller Ct values required to achieve 4 Log inactivation at a low dose, 1.5 mg L$^{-1}$ and in neutral pH range, 6.8 – 7.2 (Min et al., 2006).

Ferrate(VI) has been used as an oxidant in conjunction with coagulation for algal removal (Ma & Liu, 2002). The combined use of ferrate(VI) and alum, algal removal increased significantly in comparison with that using alum alone (Figure 3).

Although potentials of ferrate(VI) to act as coagulant, disinfectant and oxidant for water and waste water treatment have been widely investigated, researches will still be required to assess treatment efficiency and cost effectiveness considering simultaneously removing turbidity, dissolved organic carbon, particles and lowering residual iron, microbial activity in drinking water treatment and the removal of SS, COD, BOD, phosphorous and micro pollutants in waste water treatment.
2.2. Application of ferrate(VI) for emerging micro pollutant removal

The ferrate(VI) efficiency to remove 68 EDCs and PPCPs spiked in a waste water matrix were studied in two wastewater treatment plants (WWTPs) (Yang et al., 2012). Thirty-one target EDCs and PPCPs were detected in the effluents of the two WWTPs with concentrations ranging from 0.2 to 1156 ng L\(^{-1}\). Ferrate (VI) treatment resulted in selective oxidation of electron rich organic moieties of these target compounds, such as phenol, olefin, amine and aniline moieties. But ferrate(VI) failed to react with triclocarban, 3 androgens, 7 acidic pharmaceuticals, 2 neutral pharmaceuticals and erythromycin-H\(_2\)O.

In a recent study by the author's team, selected pharmaceuticals were spiked into the effluent samples with concentration of 10 μg L\(^{-1}\) for each compound. Results showed that removal efficiencies of ciprofloxacin and naproxen were up to 70% and 50%, respectively, for ferrate(VI) doses up to 5 mg L\(^{-1}\). Except ciprofloxacin and naproxen, raising ferrate(VI) dose did not improve the removal of other pharmaceutical significantly (Figure 4). The

**Fig. 1.** Comparative DOC removal, FA model water (Jiang et al., 2001)

**Fig. 2.** Inactivation level of E. coli (log(N/N\(_0\)) and exposure amount of E. coli to ferrate(VI) at various pH values (Min et al., 2006)

**Fig. 3.** Effect of ferrate(VI) oxidation on the removal of algae by alum (Ma & Liu, 2002)

**Fig. 4.** Pharmaceuticals removal by ferrate(VI) at pH 6 (Jiang and Zhou, 2013)
relative high reactivity of ciprofloxacin and naproxen with ferrate(VI) may be attributed to electron donation by the methoxy group to the naphthalene moiety (Lee et al., 2009; Yang et al., 2012). The acidic pharmaceuticals compounds (such as ibuprofen) showed less reactivity with ferrate(VI) because a carboxylic group is an electron-withdrawing functional group, which can depress the reaction of aromatic ring with ferrate(VI). Therefore, the reactivity of ferrate(VI) with carboxylic acids is usually slow.

The rate constant for the reaction of ferrate(VI) with selected EDCs and PPCPs can be seen in Table 1. The data indicate relative reaction activities between ferrate(VI) and various compounds. Ferrate(VI) can degrade most listed EDCs at rapid speed except for Buten-3-ol which has low reactivity with ferrate(VI). For the PPCPs, atenolol, carbamazepine, ibuprofen have low reactivity especially ibuprofen has the slowest reaction rate with ferrate(VI). On the other hand, the relative high reactivity of most EDCs and PPCPs with ferrate(VI) may be attributed to electron donation by the specific group to the naphthalene moiety (Lee et al., 2009; Yang et al., 2012).

Table 1. Second order rate constants \( k \), M\(^{-1}\)s\(^{-1}\) for the reaction of ferrate(VI) with selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs)

<table>
<thead>
<tr>
<th>Group</th>
<th>Contaminant</th>
<th>pH</th>
<th>Rate constant ( k ), M(^{-1})s(^{-1})</th>
<th>Half life ( t_{1/2} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endocrine disruptors</td>
<td>17(\alpha)-Ethynylestradiol</td>
<td>7</td>
<td>7.3 ( \times ) 10(^2)</td>
<td></td>
<td>(Lee et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>Bisphenol A</td>
<td>7</td>
<td>6.4 ( \times ) 10(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\alpha)-estradiol</td>
<td>7</td>
<td>7.7 ( \times ) 10(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>7</td>
<td>7.7 ( \times ) 10(^1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bisphenol-A</td>
<td>7</td>
<td>7.7 ( \times ) 10(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17(\beta)-estradiol</td>
<td>7</td>
<td>7.6 ( \times ) 10(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-methyphenol</td>
<td>7</td>
<td>6.9 ( \times ) 10(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Buten-3-ol</td>
<td>7</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPCPs</td>
<td>Atenolol</td>
<td>8</td>
<td>7</td>
<td></td>
<td>(Lee &amp; von Gunten, 2010)</td>
</tr>
<tr>
<td></td>
<td>Bisulfite</td>
<td>7</td>
<td>8.24 ( \times ) 10(^4)</td>
<td>0.2 s</td>
<td>(Sharma et al., 2011)</td>
</tr>
<tr>
<td></td>
<td>Carbamazepine</td>
<td>8</td>
<td>16</td>
<td></td>
<td>(Lee et al., 2009)</td>
</tr>
<tr>
<td></td>
<td>Ciprofloxacin</td>
<td>7</td>
<td>4.7 ( \times ) 10(^2)</td>
<td>29.4 s</td>
<td>(Lee et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>Enrofloxacin</td>
<td>7</td>
<td>4.6 ( \times ) 10(^1)</td>
<td>300 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethionine</td>
<td>8</td>
<td>8.3 ( \times ) 10(^2)</td>
<td>17 s</td>
<td>(Sharma et al., 2011)</td>
</tr>
<tr>
<td></td>
<td>Glycylglycine</td>
<td>7</td>
<td>8.2 ( \times ) 10(^2)</td>
<td>17 s</td>
<td>(Noorhasan et al., 2010)</td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>8</td>
<td>0.4</td>
<td></td>
<td>(Lee &amp; von Gunten, 2010)</td>
</tr>
<tr>
<td></td>
<td>Iodide</td>
<td>7</td>
<td>6.67 ( \times ) 10(^3)</td>
<td>2.1 s</td>
<td>(Sharma et al., 2011)</td>
</tr>
<tr>
<td></td>
<td>Sulfamethizole</td>
<td>7</td>
<td>4.1 ( \times ) 10(^2)</td>
<td>33.9 s</td>
<td>(Sharma et al., 2006)</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>7</td>
<td>1.3 ( \times ) 10(^3)</td>
<td>10.4 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfisoxazole</td>
<td>7</td>
<td>1.5 ( \times ) 10(^3)</td>
<td>9.2 s</td>
<td></td>
</tr>
</tbody>
</table>

3. ASSESSMENT OF THE TOXICITY OF FERRATE(VI) TREATED WATER AND WASTE WATER

In order to relieve public health concerns when a new chemical is employed for water treatment it is important to determine whether the ferrate(VI) treated water contains any toxic or mutagenic substances. The Ames test has been applied to ferrate(VI) treated water and a preliminary study demonstrated negative results (DeLuca et al., 1983), suggesting that
ferrate(VI) reagents do not produce mutagenic by-products for the study conditions. Moreover, in a recent study (Jiang et al., 2013), the toxicity of the ferrate(VI) treated waste water effluent was assessed and compared with that of raw waste water effluent by the zebrafish embryos model. The zebrafish embryos represent an attractive model for environmental risk assessment of chemicals since they offer the possibility to perform small-scale, high-throughput analyses. The results of both mortality of zebrafish embryo tests and microscopic images demonstrated that raw waste water effluents possessed toxicity to zebrafish but ferrate (VI) treated effluents had no adverse effects (Figure 5).

Fig. 5. Effects of effluents on zebrafish embryos hatching after the treatment for 72 h. Raw effluent (100%) and ferrate (1, 2 or 3 mg Fe L\(^{-1}\)) treated effluent were diluted to 75%, 50% and 25% with zebrafish embryo water for the treatments, zebrafish embryo water was as a control sample. Results are shown as the mean ± SD (n=7). ** represents p<0.01; * represents p<0.05; Error bar: standard deviation (SD) (Jiang et al., 2013).

A number of other studies have reported the potential formation of harmful by-products (Table 2). Most recently, a study showed the formation of adsorbable organic haloids (AOX) in the ferrate(VI) treated waste water effluents although the AOX concentration rise was lower than that in the chlorination process (Gombos et al., 2013). Obviously, more researches need carried out to investigate the formation potential of harmful by-products during ferrate(VI) treatment. For example, it is to be studied under which operating conditions and for which original pollutants, that harmful by-products would be formed.

Table 2. Harmful by products formation in the ferrate(VI) treated waste water

<table>
<thead>
<tr>
<th>Compound</th>
<th>By-product</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrates</td>
<td>Aldehydes</td>
<td>(BeMiller et al., 1972)</td>
</tr>
<tr>
<td>Aniline</td>
<td>Azobenzene and Nitrobenzene</td>
<td>(Huang et al., 2001)</td>
</tr>
<tr>
<td>Phenol</td>
<td>Pbenzoquininone and Biphenols</td>
<td>(Huang et al., 2001)</td>
</tr>
<tr>
<td>Methanol</td>
<td>Formaldehyde</td>
<td>(Rush et al., 1995; Ohta et al., 2001)</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>Aldehyde, Ketone, and Carboxyl groups</td>
<td>(Sharma, 2013)</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Methyl group compounds</td>
<td>(Sharma et al., 2006)</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>3,4,5-trimethoxybenzaldehyde and 2,4-dinitropyrimidine</td>
<td>(Anquandah et al., 2011)</td>
</tr>
</tbody>
</table>
4. FEASIBILITY OF FERRATE(VI) TREATMENT IN FULL SCALE WATER AND WASTE WATER TREATMENT

The advances in analytical chemistry theory and instrument allow tiny and low level concentrations of micro-pollutants could be detected which helps the new legislated regulations could be setup and quality of water could be monitored. Water industries have to meet the requirement of stringent water and waste water quality regulations and therefore, alternative technologies are sought by water industries.

A number of laboratory based studies have investigated using ferrate(VI) as a water treatment chemical to degrade micro pollutants including the reaction schemes and mechanisms, possible by-products formation, and kinetics or rate constants; these have advanced knowledge of the use of ferrate(VI) for the environmental remediation. In comparison with these fundamental studies, relative smaller number researchers have focused on the practical application of ferrate(VI) for water and waste water treatment or the environmental remediation such as odour removal and sewage sludge treatment. Nevertheless, a few of cases have been reported that ferrate(VI) have been used in full scale applications so far.

Studies on the overall efficiency of ferrate(VI) as a coagulant, an oxidant or a disinfectant have been carried out for water and waste water treatment. However, there are some fundamental issues which have not yet been studied thoroughly and are critical to implement ferrate(VI) into full-scale water treatment and other environmental remediation.

This author suggests following future work to be carried out:

1) To classify and assess the toxicity of the potential degraded by-products when ferrate(VI) is used to oxidize various micro-pollutants;
2) To study the effects of dosing points, dosing methods, dosing farcicalities and mixing schemes on the ferrate(VI) performance in water and wastewater treatment;
3) To investigate the impact of water quality characteristics on the ferrate(VI) efficiency as a disinfectant and as an oxidant;
4) To assess the effect of ferrate(VI) dose and pH on the reduction of various micro-pollutants and on the inactivation of bacteria and virus in sewage sludge treatment, and finally;
5) To carry out a full-scale trial to validate the treatment performance obtained in the laboratory studies and to evaluate economic suitability of using ferrate(VI) comprehensively.

REFERENCES


