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Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents

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ABSTRACT

We investigated the removal efficiencies of 68 selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) spiked in a wastewater matrix by ferrate (Fe(VI)) and further evaluated the degradation of these micropollutants present in secondary effluents of two wastewater treatment plants (WWTPs) by applying Fe(VI) treatment technology. Fe(VI)treatment resulted in selective oxidation of electron-rich organic moieties of these target compounds, such as phenol, olefin, amine and aniline moieties. But Fe(VI) failed to react with triclocarban, 3 androgens, 7 acidic pharmaceuticals, 2 neutral pharmaceuticals and erythromycin-H_2O.Thirty-one target EDCs and PPCPs were detected in the effluents of the two WWTPs with concentrations ranging from 0.2 ± 0.1 ng L^{-1} to 1156 ± 182 ng L^{-1}.Fe(VI) treatment resulted in further elimination of the detected EDCs and PPCPs during Fe(VI) treatment of the secondary wastewater effluents. The results from this study clearly demonstrated the effectiveness of Fe(VI) treatment as a tertiary treatment technology for a broad spectrum of micropollutants in wastewater.

1. Introduction

Endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) have been found incompletely removed in various conventional wastewater treatment plants (WWTPs) (Ying et al., 2008, 2009a; Liu et al., 2009; Khetan and Collins, 2007). Wide presence of EDCs and PPCPs in WWTP effluents and in receiving aquatic environments may affect water quality and pose potential risks to aquatic organisms and human health (Ying et al., 2009b; Khetan and Collins, 2007; Witorsch and Thomas, 2010). WWTP effluents have been considered as an important source of micropollutants for aquatic environments; therefore advanced treatment technologies such as ozonation (Nakada et al., 2007; Hollender et al., 2009; Zimmermann et al., 2011) and activated carbon filtration (Nowotny et al., 2007) are required to reduce the emission of micropollutants via WWTPs effluents. One alternative advanced oxidation technology is ferrate (Fe(VI)) treatment technology.

Fe(VI) is a supercharged iron molecule in which iron is in the +6 oxidation state. Due to its dual functions of an oxidant and a subsequent coagulant/precipitant as ferric hydroxide (Fe(III) $(OH)_3$) (Ma and Liu, 2002), Fe(VI) is regarded as an environmentally friendly oxidant in water and wastewater

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treatment process (Jiang and Lloyd, 2002; Sharma, 2002; Lee et al., 2004). However, Fe(VI) solutions are generally unstable, while solid Fe(VI) salts are stable when their contact with ambient air is avoided. In addition, Fe(VI) salts are costly as their production requires multiple chemical processes and long time synthesis, which has limited its use in water and wastewater treatment applications (Jiang and Lloyd, 2002; Sharma, 2002). But recent development in the in situ production of Fe(VI) using an electrochemical method makes it a promising oxidant for the practical application in water and wastewater treatment plants (Yu and Licht, 2008; Alsheyab et al., 2009; Macova et al., 2009).

Fe(VI) has been demonstrated to be very promising in the removal of suspended solids, phosphate, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) at a very low dose in comparison with a normal coagulant of ferric sulphate (Jiang et al., 2006, 2009). At the same time, Fe(VI) can remove various micropollutants in a single treatment step due to its reactivity with electron-rich moieties such as phenols, anilines, amines and olefins of organic pollutants (Lee et al., 2009; Lee and von Gunten, 2010). However, research into the removal of micropollutants in secondary wastewater effluents, especially EDCs and PPCPs in effluents by Fe(VI), is still very limited.

The objectives of this study were (i) to assess the removal efficiencies of 68 selected EDCs (7 estrogenics, 14 androgens, 5 progestagens and 5 glucocorticoids) and PPCPs (17 antibiotics, 14 acidic pharmaceuticals, 4 neutral pharmaceuticals and 2 antimicrobial agents) spiked into a secondary wastewater effluent to yield concentrations higher than occurring environmental concentrations by Fe(VI),and (ii) to further evaluate the degradation of these micropollutants at concentrations naturally occurring in two secondary effluents by applying Fe(VI) treatment technology. This is the first paper to investigate the removal of androgens, progestagens and glucocorticoids by Fe(VI).

2. Experimental section

2.1. *Standards and materials*

The standards of 68 selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) and their corresponding 19isotope-labeled internal standards with high purities (98.0%–99.9%)were purchased from various chemical suppliers. The chemical structures of these target compounds are provided in Supporting Information (Figures S1–S4), and their detailed information is referred to Liu et al. (2011), Chen et al. (2010), Yang et al. (2011a) and Zhao et al. (2009).

Potassium ferrate (Fe(VI)) was prepared by wet chemical synthesis (Delaude and Laszlo, 1996), with a purity of above 95% as Fe(VI) (w/w). All organic solvents used in the following sample processing and analysis were of HPLC grade and obtained from Merck Corporation (Shanghai, China) or CNW Technologies (Dusseldorf, Germany). HPLC grade water was obtained from a Milli-Q water purification system (Millipore, Watford). Oasis HLB cartridges (500 mg, 6 mL) were supplied by Waters Corporation (Milford, MA, USA). The individual standard solutions as well as internal standard solutions (100 mg L^{-1}) were prepared in methanol and stored in amber glass bottles at −18 °C. Working solutions of these target compounds were prepared fresh from their stock solutions by serial dilution.

2.2. *Elimination experiment of selected EDCs and PPCPs spiked in a wastewater matrix by Fe(VI)*

According to instrumental analysis methods, 68 selected micropollutants were divided into 5 groups: Group 1 (14 androgens, 5 progestagens and 5 glucocorticoids) (Liu et al., 2011); Group 2 (7 estrogenics, 2 antimicrobial agents) (Chen et al., 2010); Group 3 (17antibiotics) (Yang et al., 2011a); Group 4 (14 acidic pharmaceuticals) (Chen et al., 2010) and Group 5 (4 neutral pharmaceuticals) (Chen et al., 2010). Elimination experiment of 68 selected micropollutants was performed in a secondary wastewater effluent (dissolved organic carbon (DOC) of 5 mg C L^{-1}) spiked with each group of micropollutants and treated by Fe(VI) as a function of Fe(VI) exposure at 23 ± 2 °C and pH 7.0 (10 mM bicarbonate buffer). The Fe(VI) exposure represents the time integrated concentration of Fe(VI). For the characteristics of the effluent, please see Text S1. In the 100 mL reaction mixture solutions, the initial concentration of Fe(VI) was set at 10 mg Fe L^{-1} while the concentration for each of selected micropollutants was 100 μg L^{-1}. The experiment was performed in a 150 mL beaker equipped with a magnetic stirrer (500 r min^{-1}). Reactions were initiated by adding the solid Fe(VI) to suspensions containing each group of micropollutants under rapid mixing. At certain time intervals, 1 mL of the reaction solution was sampled and quenched with a diammonium 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS) solution to measure residual Fe(VI) concentrations (Fig. S5) using an ABTS method at 415 nm (Lee et al., 2005a), and 0.8 mL of the reaction solution was quenched with a thiosulfate solution (10 mM, 0.1 mL), and followed by addition of corresponding internal standards (1 mg L^{-1}, 0.1 mL), then the treated samples were filtered through a 0.45 μm PTFE filter (Shanghai ANPEL, China) and subjected to the instrumental analysis within 24 h. Preliminary experiment showed that the trace pollutants in wastewater, quenching processes and PTFE filtration did not interfere with the experiments. Each experiment was conducted in duplicate.

2.3. *Application of Fe(VI) for wastewater treatment*

Fe(VI) treatment of wastewater effluents in terms of removal of selected EDCs and PPCPs was carried out by applying solid Fe(VI) to secondary wastewater effluents at an initial pH value of 6.88 and 7.09 for Plant A and Plant B respectively and at the room temperature (23 ± 2 °C).Detailed information about the two sewage treatment plants and collection of effluent samples is given in Text S2. In a series of 1 L secondary wastewater effluent, the solid Fe(VI) was dosed to yield concentrations of 0, 2.5, 5 and 10 mg Fe L^{-1}. The solutions were stirred initially and then allowed to react for 3 h in the dark. The decrease of Fe(VI) in the secondary effluent of Plant A and Plant B is shown in Fig. S6 and Fig. S7. After complete reaction, 50 mL of methanol and 400 μL 4 M H_2SO_4 were added to each