Korean J. Chem. Eng., 34(3), 734-740 (2017)
DOI: 10.1007/s11814-016-0324-y

pISSN: 0256-1115
eISSN: 1975-7220

Efficient oxidative removal of 4-tert-octylphenol and 17α-ethynylestradiol from aqueous solutions using ferrate(VI)

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(*Received 20 June 2016 • accepted 20 November 2016*)

Abstract−Ferrate(VI) was utilized to treat micro-pollutants--4-tert-octylphenol (TOP) and 17α-ethynylestradiol (EE2)--from aqueous solutions. Batch studies were conducted at various pHs (7.0 to 12.0) and concentrations of TOP/ or EE2 (0.03 to 0.3 mmol/L) using 0.1 mmol/L ferrate(VI). Time-dependent degradation of TOP and EE2 was assessed as a function of pH and micro-pollutant concentrations and we found that significant mineralization of micro-pollutants was achieved by ferrate(VI) treatment. Second-order kinetics showed 1 : 1 stoichiometry was obtained between the ferrate(VI) and TOP/or EE2. Further, the effect of several background electrolytes on degradation of TOP and EE2 by ferrate(VI) was evaluated, showing insignificant effect of degradation.

Keywords: Ferrate(VI), 4-Tert-octylphenol, 17α-Ethynylestradiol, Endocrine Disruptors, Mineralization, Background Electrolytes

INTRODUCTION

Organic micropollutants are considered a serious environmental threat because the micropollutants are persistent in nature, poorly biodegradable, and found toxic even at low concentrations [1]. The presence of several micropollutants, including many pharmaceutical and personal care products (PPCPs) in the terrestrial environment, has been widely demonstrated by several monitoring agencies. Notably, there are measurable concentrations of several micropollutants in wastewater, surface water, sediments, groundwater, and even in drinking water [2-4]. Most micropollutants enter the terrestrial environment through direct runoff and excretion of unmetabolized drugs or active metabolites and/or degradation byproducts [5]. Conventional sewage/waste water treatment systems are unable to eliminate completely these micropollutants, resulting in residual loads of pollutants in effluent water [6]. Therefore, effluents of wastewater treatment plants are considered to be important sources of micropollutants in the water bodies [7-9].

Alkylphenol polyethoxylates, which are non-ionic surfactants, are commonly used as detergent, emulsifiers, and dispersing agents [10-12]. However, biological degradation of these surfactants in waste water treatment plants yields alkylphenols as metabolites. These alkylphenols possess greater toxicity, estrogenic activity, and are more persistent in the aquatic environment than the parent molecules [13-15]. 4-Tert-octylphenol, one of the breakdown products of alkylphenol polyethoxylates, shows the strongest estrogenic properties among the breakdown products; it is approximately five-times more estrogenic than nonylphenol [16,17]. Several reports have demonstrated that octylphenols or nonylphenols bioaccumulate in the lipids of water organisms [18,19]. Similarly, 17α-ethynylestradiol (EE2) is a synthetic estrogen that is a derivative of the natural hormone estradiol. EE2 is a key ingredient in oral contraceptives used by women and is also used as a hormonal agent in the stockbreeding industry [1,20,21]. EE2 is one of the most potent endocrine disruptors due to its powerful estrogenic activity [22], and hence poses a serious environmental threat even at low levels in aqueous solutions.

Ferrate(VI) possessed with +6 oxidation state of iron is highly unstable in aqueous solutions [23-26]. This is because of the high redox potential of Fe(VI) ($E^0_{Fe(VI)/Fe(III)}$: 2.20 (pH: 1.0) and $E^0_{Fe(VI)/Fe(III)}$: 0.72 (pH: 14)). Reduction of ferrate(VI) leads to the formation of ferric(III) in aqueous solution, which is a fairly good coagulant which coagulates efficiently the non-degradable impurities from aqueous solutions. Therefore, ferrate(VI) shows a multifunctional role in wastewater treatment. Moreover, ferrate(VI) treatment is devoid of formation of toxic by-products, and hence considered as a safe, environmentally-friendly chemical for such operations [27-30]. Ferrate(VI) is successfully employed for oxidative degradation of PPCPs from aqueous solutions [9]. Surface water or wastewater treatment effluents were spiked with the micro-pollutants of bisphenol A, EE2, and E2 and then treated with ferrate(VI) at pH 8.0. Within 30 min of contact, 99% removal of these pollutants was achieved and pseudo-second order rate kinetics was obtained in the degradation process [31]. Significant concentrations of endocrine disrupting chemicals (EDCs), bisphenol A, estrone, and 17β-estradiol, has been detected in wastewater treatment works (WwTWs), and preliminary treatment with ferrate(VI) lowers significantly the chemical oxygen demand (COD) value of wastewater, which indi-

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cates a significant decrease in pollutant load in the treated water [32,33]. Similarly, the reactivity of ferrate(VI) towards five important EDCs, bisphenol A, 17α-ethynylestradiol (EE2), estrone (E1), β-estradiol (E2), and estriol (E3), was carried out at a wide range of pH 8-12. The kinetics of degradation along with possible intermediates was identified in the treatment process [34]. Weakly acidic condition, pH 5.0-6.0, was found to be optimal for the complete removal of BPA from aqueous solutions; however, several intermediates having phenyl ring were detected. Moreover, the co-existing humic acids and SiO_3^{2-} inhibited BPA degradation, although HCO_3^- slightly favored BPA degradation by ferrate(VI) [35].

Similarly, the anti-bacterial drug sulfamethoxazole was treated with ferrate(VI) and an extensive kinetic study was carried out at wide range of pH (6.93-9.50) and temperature (15-45 °C). An apparent second-order rate constant decreased from $1.33\pm0.08\times10^{-3}$ M^{-1} s^{-1} to $1.33\pm0.10\times10^{0}$ M^{-1} s^{-1} with the increase in pH from 7.0 to 9.50 [36]. The degradation mechanism and kinetics of degradation of organo-sulfur compounds and propanol by ferrate(VI) in aqueous solutions was investigated [37,38]. Ferrate(VI) electrophilically attacks the benzotriazoles at the 1,2,3-triazole moiety of BT (1H-benzotriazole), 5MBT (5-methyl-1H-benzotriazole), DMBT (5,6-dimethyl-1H-benzotriazole hydrate), and 5CBT (5-chloro-1H-benzotriazole), whereas an attack at the N-OH bond of HBT (1-hydroxybenzotriazole) results in the degradation of several benzotriazoles by ferrate(VI). The protonated species $HFeO_4^-$ is relatively more reactive than the unprotonated FeO_4^{2-} species of ferrate(VI) [39]. Ciprofloxacin, a high priority antibiotic drug, was treated with ferrate(VI) and at least 60% of the drug was removed from wastewater at ferrate concentration of <0.3 mg/L [40]. These studies show the potential applicability of ferrate(VI) in the remediation of wastewaters contaminated with micropollutants. Therefore, the present study intended to treat systematically the two important micro-pollutants, 4-tert-octylphenol (TOP) and 17α-ethynylestradiol (EE2), from aqueous solutions under the simulated wastewater conditions. The study was conducted for various parametric studies: the effect of pH (pH 7.0 to 12.0), concentration of micro-pollutants (0.03 to 3.0 mmol/L) and presence of several interfering ions.

MATERIAL AND METHODS

1. Materials

4-Tert-octylphenol (structure 1), 17α-ethynylestradiol (structure 2), iron(III) nitrate nanohydrate, diethyl ether, and hexane were procured from Sigma Aldrich. Co., USA. Potassium hydroxide, hydrochloric acid, and phosphoric acid were obtained from Merck India Ltd., India. Disodium tetraborate decahydrate and disodium hydrogen phosphate were obtained from Himedia India Ltd., India. Purified sodium hypochlorite was obtained from Palanad Enterprises, Nagpur, India. Purified water (10-15 MΩ cm) was obtained using a Millipore Water Purification system (Elix 3).

2. Methods

2-1. Preparation of Potassium Ferrate(VI)

Potassium ferrate(VI) was prepared by using the wet chemical oxidation process, with modifications described previously [21,28,30]. The purity of the prepared ferrate(VI) was found to be above 95%. Ferrate(VI) was always prepared freshly. The product was carefully kept in a vacuum desiccator that contained NaOH pellets.

2-2. Batch Reactor Method

1.0 mmol/L TOP and EE2 stock solutions were prepared by dissolving an appropriate amount of TOP or EE2 separately using phosphate/borate (0.01 mol/L) buffer solutions. The required pH was obtained by dropwise addition of phosphoric/sodium hydroxide (0.1 mol/L) solutions. The required concentration of TOP or EE2 was obtained by successive dilution of stock solutions. Batch reactor operations were carried out at various concentrations of TOP or EE2 (0.03 to 0.3 mmol/L; 100 mL each) and at various pH values (pH 7.0 to 12.0) in a reactor vessel, and then a constant amount of solid potassium ferrate (equivalent to 0.1 mmol/L) was introduced in the reactor vessel under stirred condition. Decomposition of ferrate(VI) was measured in tandem with the degradation of TOP or EE2. Once after the introduction of ferrate(VI), the absorbance of the stirred solution was immediately measured at 510 nm at regular time intervals at least for 20 min (UV-visible spectrophotometer: Thermo Electron Corporation, England; Model: Thermo Spectronic UVI). In parallel, the absorbance of a blank solution, having an identical ferrate(VI) concentration and pH (no TOP or EE2), was recorded for applicable blank corrections. Using this blank data, necessary absorbance correction was conducted to account for the self-degradation of ferrate(VI). Samples were kept in the reactor for another 2 hrs under stirred conditions. It was then filtered using a syringe filter (0.45 μm) and subjected to high performance liquid chromatography and total organic carbon analysis (TOC-VCPH/CPN analyzer, Shimadzu, Japan).

HPLC measurements were conducted using the Waters HPLC instrument (Waters 515 HPLC pump) equipped with a Waters 2489 UV/visible detector and C18 5 μm (4.6×250 mm) column. The flow rate was maintained at 1.0 mL/min for an injected volume of 20 μL. The mobile phase acetonitrile : water (70 : 30) for EE2 and acetonitrile : water : acetic acid (glacial) (70 : 29 : 1) for TOP was used. The absorbance of TOP was recorded at 222 nm and that of EE2 at 280 nm. The peak area was used to calculate the concentration of TOP or EE2. Standard solutions of TOP and EE2 were prepared by dissolving an appropriate amount of TOP or EE2 in HPLC-grade water (Merck, India). The peak area was also used to obtain the percent removal of TOP or EE2. Results were presented as the percent of TOP or EE2 removed as a function of TOP or EE2 concentration and pH.

Mineralization of the micropollutants was assessed by total organic carbon (TOC) measurement, which was then converted into percent removal using the initial TOC value of TOP or EE2. Total percent removal of TOC is indicative of the percent mineralization of these pollutants from aqueous solutions. The percent mineralization of TOP or EE2 was obtained and presented as a function of TOP or EE2 concentration at the studied pH. Moreover, the difference in TOC values, i.e., between the initial and treated samples, was utilized to calculate the amount of TOP or EE2 removed, and was presented as a function of pH and initial pollutant concentration.

Degradation of TOP and EE2 was also conducted in presence of several background electrolytes: Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$, and Na_2SO_3. The concentration of background electrolytes, TOP or EE2, and ferrate(VI), was set to 0.1 mmol/L, and samples were treated at pH 8.0. Solutions were stirred for 2 hrs and then filtered using syringe filter (0.45 μm) and TOP or EE2 concentrations were estimated using HPLC.

RESULTS AND DISCUSSION

1. Batch Reactor Analysis

1-1. Effect of pH and Concentration of 4-Tert-octylphenol and 17*α*-Ethynylestradiol

TOP and EE2 solutions were treated by ferrate(VI) at varied pHs (pH 7.0 to 12.0) and at wide range of ferrate(VI) to TOP or EE2 molar ratios (from 1 : 0.3 to 1 : 3). Thus, TOP or EE2 concentrations were increased from 0.03 mmol/L to 0.3 mmol/L at a constant dose of ferrate(VI) 0.1 mmol/L. The results for TOP or EE2 at pH 8.0 are illustrated in Figs. 1(a) and 1(b), respectively. It is evident that increasing the concentration of TOP or EE2 caused an enhanced reduction of ferrate(VI). This indicated that the degradation of pollutant was increased significantly at higher pollutant concentration. Further, the ferrate(VI) concentration decreased sharply during the initial period of contact, after which an apparent equilibrium was achieved or a constant ferrate(VI) concentration was obtained. A maximum decrease in ferrate(VI) concentration was observed within the initial *Ca* 5~8 min of contact for these two pollutants. This clearly indicated that ferrate(VI) was efficient in the degradation of TOP or EE2 in aqueous solutions. Quantitatively, increasing the contact time from 0 to 20 min, the amount of ferrate (VI) was decreased from 0.10 to 0.022 mmol/L for TOP and from 0.10 to 0.060 mmol/L for EE2 at 1 : 1 molar ratios of ferrate(VI) and micro-pollutant. It was reported previously that EE2, which possesses a pk_a value of 10.3, remained undissociated in aqueous solution even up to pH value of ~10.0 [41]. Similarly, 4-tert-octylphenol behaves like a weak acid with a pk_a value of ~10.0. Therefore, TOP is also present in the environment with its undissociated species and found to be more hydrophobic chemical form [42]. This is the reason the EE2 and TOP are relatively stable in an aquatic environment and are resistant to biodegradation [43]. Rapid degradation of TOP and EE2 by ferrate(VI) highlights the high reactivity of ferrate(VI) towards EDCs in aqueous media [32].

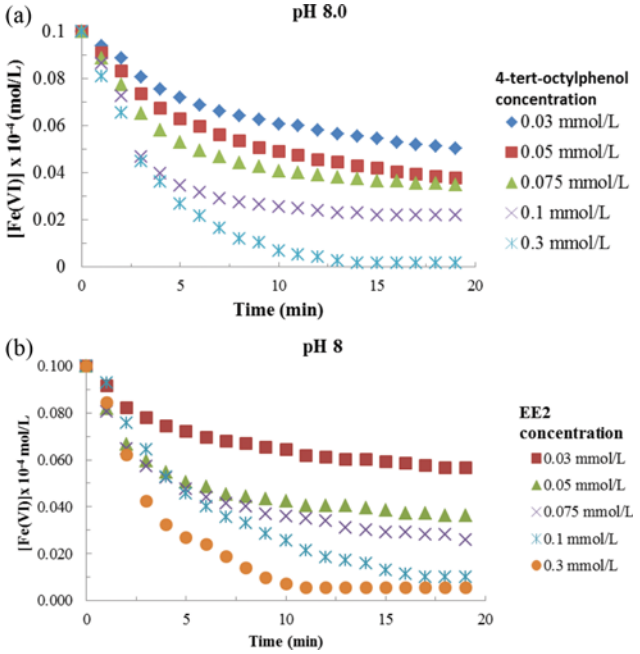

Fig. 1. Time dependence degradation of (a) 4-tert-octylphenol; and (b) 17*α*-ethynylestradiol by ferrate(VI) as a function of pH and concentrations of TOP or EE2.

1-2. Kinetic Studies

Kinetic studies of micro-pollutant degradation by ferrate(VI) were conducted by using the time dependence change in ferrate(VI) concentration at pH 8.0. The rate of ferrate(VI) reduction in presence of micro-pollutants could be presented as Eq. (1):

$$-\frac{\mathrm{Fe(VI)}}{\mathrm{dt}}=\mathrm{k}_{app}[\mathrm{Fe(VI)}]^{m}[\mathrm{MP}]^{n} \tag{1}$$

where k_{app} is an apparent rate constant in degradation of ferrate(VI) in presence of micro-pollutant TOP/or EE2. At varied concentrations of TOP/or EE2 and at constant pH, the above equation is reduced to Eq. (2):

$$-\frac{\mathrm{Fe(VI)}}{\mathrm{dt}}=\mathrm{k}[\mathrm{Fe(VI)}]^{m} \tag{2}$$

$$\text{where, } \mathrm{k}=\mathrm{k}_{app}[\mathrm{MP}]^{n} \tag{3}$$

The time dependence change in ferrate(VI) concentration is utilized to fit into the pseudo-first-order rate and pseudo-second-order rate equations to optimize the value of 'm' either one or two at pH 8.0. It is observed that the kinetic data is reasonably fitted well to the pseudo-first order rate kinetics, which clearly indicates the value of 'm' is 1 with respect to the degradation of ferrate(VI) in presence of TOP/or EE2. The pseudo-first order rate constant values at pH 8.0 were obtained and illustrated in Table 1 with the

Table 1. Pseudo-second order rate constants estimated in the degradation of ferrate(VI) in presence of micro-pollutants at pH 7.0

Concentration of TOP/or EE2 (mmol/L)	Pseudo-first order rate constant (min^{-1})			
	4-Tertoctyl phenol		17*α*-Ethynylestradiol	
	$kx10^{-2}$	R^2	$kx10^{-2}$	R^2
0.03	4.72	0.956	3.55	0.911
0.05	6.66	0.967	6.61	0.886
0.075	8.18	0.935	7.74	0.908
0.10	12.78	0.861	13.79	0.981
0.30	26.30	0.996	24.78	0.977

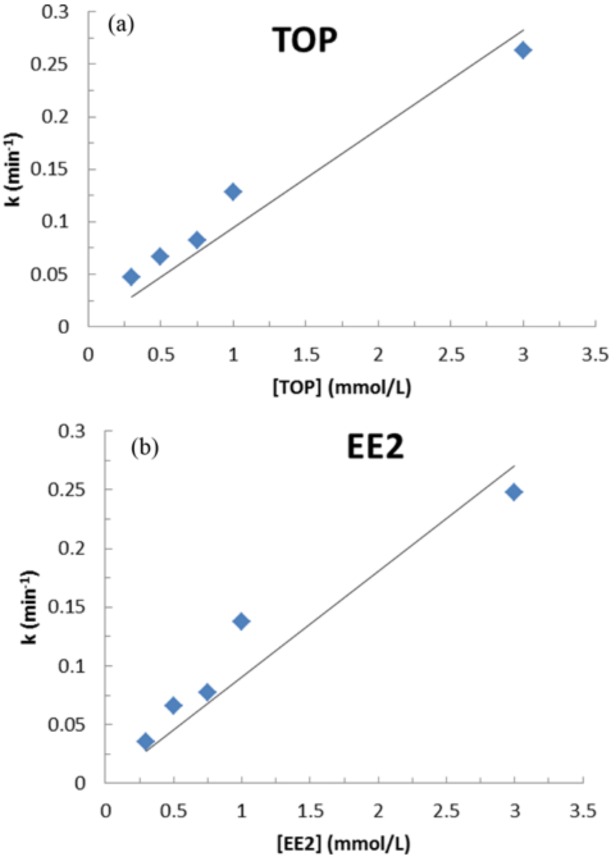

Fig. 2. Variation of pseudo-first order rate constants (k) as a function of (a) TOP; and (b) EE2 at pH 8.0.

regression coefficient (R^2). Clearly, increasing the pollutant concentration (from 0.03 to 0.3 mmol/L) apparently increases the pseudo-first order rate constant values for both the micro-pollutants. This is perhaps due to the fairly high oxidizing capacity of ferrate(VI) towards the pollutants that enables faster oxidation of the pollutant species in aqueous solutions [44].

The value of 'n' along with the apparent rate constant value k_{app} was obtained by using the pseudo-first order rate constant values obtained at varied concentrations of TOP/or EE2 at pH 8.0. A plot was drawn between the concentrations of TOP/or EE2 against the estimated values of 'k' and shown in Fig. 2 separately for TOP and EE2. Fig. 2 clearly shows that reasonably good linearity is obtained between the concentration of TOP/or EE2 against the k values at pH 8.0. Hence, this indicates the value of 'n' is found to be 1. These results indicate that the stoichiometric ratio of the ferrate(VI) and TOP/or EE2 is found to be 1 : 1. Further, the apparent rate constant k_{app} was obtained as 94.07 (r^2=0.921) and 90.17 (r^2=0.879) L/mol/min, respectively, for TOP and EE2. The values of k_{app} obtained for the TOP and EE2 were comparable to each other. Moreover, relatively high value of k_{app} indicates that the ferrate(VI) is efficient in the degradation of both the micro-pollutants from aqueous solutions [45,46].

1-3. Effect of pH on the Degradation of Micro-pollutants with Ferrate(VI): HPLC Measurements

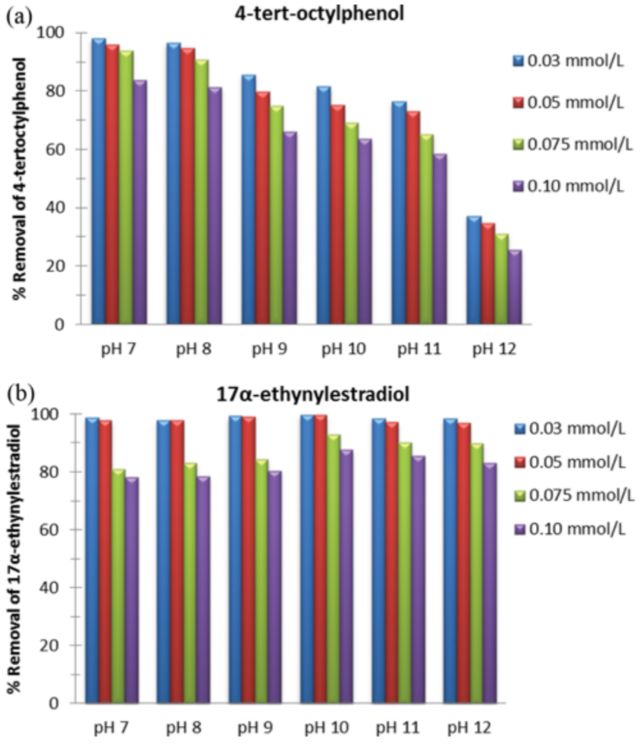

Fig. 3. Percent removal of (a) 4-tert-octylphenol; and (b) 17α-ethynylestradiol as a function of solution pH and pollutant concentrations using a constant dose of ferrate(VI) of 0.1 mmol/L.

The pH-dependent degradation of both micropollutants is an important parameter to consider the applicability of ferrate(VI) in the degradation of micropollutants from aqueous solution efficiently. Moreover, it allows a further inference of a plausible mechanism involved in the degradation process. Degradation of micropollutants was studied using HPLC measurements and the results are shown in Fig. 3 as the percent removal of TOP or EE2 as a function of pH and micropollutant concentrations. In general, increasing the concentration of the micropollutant decreased the percent removal of the micro-pollutant at a constant concentration of ferrate(VI). More quantitatively, increasing the TOP concentration from 0.03 to 0.1 mmol/L decreased the percent removal of TOP from 98.04 to 83.84%, respectively, at pH 7.0 at a ferrate(VI) concentration of 0.1 mmol/L. Similarly, removal of EE2 decreased from 98.73 to 78.13% for an increase in EE2 concentration from 0.03 to 0.1 mmol/L at pH 7.0, at the ferrate(VI) dose of 0.1 mmol/L. The decrease in percent removal at higher pollutant concentrations was because at lower concentrations of micropollutant, there were relatively more ferrate(VI) molecules present to degrade a lesser number of micro-pollutant molecules. However, at higher concentrations of micropollutants, there were relatively more TOP or EE2 molecules available for the degradation by the same number of ferrate(VI) molecules. This resulted in a higher percent removal of micropollutant molecules at lower initial concentrations of TOP or EE2 from aqueous solutions, which was gradually decreased with an increase in pollutant concentration. Further, the basic assumption of degradation of micro-pollutants is depicted as:

$$\mathrm{Fe(VI)+MC \rightarrow Fe(III)+Oxidized\ Products+CO_2} \tag{4}$$

It was found that ferrate(VI) could partly oxidize the TOP or EE2 from aqueous solutions since a partial decrease in TOC values was observed with the treated samples. However, a significant decrease in TOP or EE2 was observed, indicating that the TOP or EE2 was oxidized significantly by a single dose treatment of ferrate(VI).

It was further observed that a decrease in pH from 12.0 to 7.0 favored degradation of TOP (*cf* Fig. 3). Quantitatively, decreasing the pH from 12.0 to 7.0 increased the corresponding percent degradation of TOP from 25.47 to 83.84% at the ferrate(VI) to TOP molar ratio of 1 : 1. Speciation studies conducted previously showed that at around pH 7.0, the protonated species of ferrate(VI), i.e., $HFeO_4^-$, is the predominant species because the pk_a value for the acid dissociation of $HFeO_4^-$ is 7.3 [45,47]:

$$HFeO_4^- \leftrightarrow FeO_4^{2-} \quad (pk_a=7.3) \tag{1}$$

The reactivity of the protonated ferrate(VI) species was higher than that of the unprotonated species because the protonated species possessed greater spin density [48-51]. The redox potential of ferrate(VI) also gradually increased with a decrease in pH. This highlights the increased reactivity of ferrate(VI) at lower pH values [23,24]. It was reported previously that the degradation of various steroid estrogens, including BPA, was significantly enhanced at lower pH conditions because of the presence of more of the reactive protonated species of ferrate ($HFeO_4^-$) than the deprotonated species (FeO_4^{2-}) [34].

The very high degradation of EE2 by ferrate(VI) was almost unaffected by a change in pH from pH 7.0 to 12.0. Approximately 80% of EE2 was degraded by ferrate(VI) for a 1 : 1 Fe(VI) to EE2 molar ratio. This clearly demonstrated the high reactivity of ferrate(VI) towards EE2 in aqueous media. Previously, a small variation in rate of degradation of glycine by ferrate(VI) was observed within the increase in pH 6.0 to 8.0. This dependence of the reactivity of ferrate(VI) with glycine reacts differently with ferrate(VI) under the studied pH conditions [52].

2. Mineralization of Micro-pollutants

The possible mineralization of micropollutants by ferrate(VI) treatment was assessed by using the total carbon analysis. This data further could be utilized in ultimate implication of ferrate(VI) technology in real wastewater treatment method. Samples of micropollutants, TOP and EE2, at different initial concentrations (0.03 to 0.1 mmol/L) were treated with a constant dose of ferrate(VI) for 2 hrs at various pH (pH 7.0 to 12.0) conditions. Samples were then filtered, and total organic carbon (TOC) values along with those of blank samples were measured. The percent TOC removal of the micropollutant was obtained as a function of pollutant concentration and solution pH, and is illustrated in in Figs. 4(a) and 4(b) for TOP and EE2, respectively. It is clear from these figures that a decrease in micropollutant concentration and pH greatly favored the removal of TOC. More quantitatively, decreasing the micropollutant concentration from 0.1 to 0.03 mmol/L increased the TOC removal from 30.54 to 75.99% (for TOP) and from 22.42 to 43.15% (for EE2), respectively, at pH 7.0. In contrast, decreasing the solution pH from 12.0 to 7.0 increased the percent TOC removal of TOP from 13.99 to 30.54% at a 1 : 1 molar ratio of ferrate(VI) to micro-pollutant. This again reaffirmed that ferrate(VI) reactivity was higher at lower pH values. However, mineralization of EE2 was not significantly affected by a change in pH from 7.0 to 12.0. These results are consistent with the HPLC measurements; percent removal of EE2 was almost unaffected by a change in pH. Further, the TOC data clearly indicated that although partial mineralization of these micropollutants occurred, a significant percent of the TOP and EE2 was, perhaps, mineralized with a single dose of ferrate(VI).

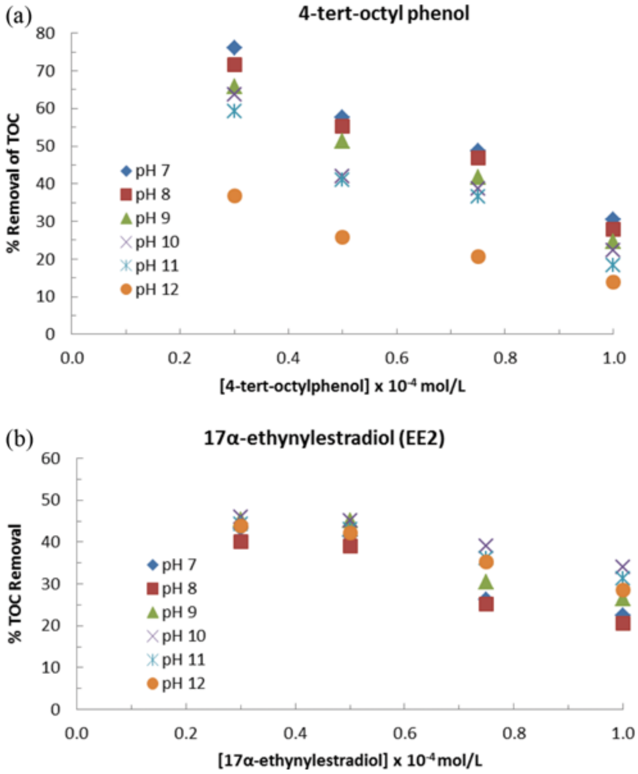

Fig. 4. Percent TOC removal of (a) 4-tert-octylphenol and (b) 17*α*-ethynylestradiol (EE2) as a function of pH and the initial concentration of micro-pollutants [Ferrate(VI) dose: 1.0×10^{-4} mol/L].

3. Effect of Background Electrolytes

The effect of the presence of co-existing ions on the oxidative removal of TOP or EE2 (0.1 mmol/L) using ferrate(VI) dose of 0.1 mmol/L at pH 8.0 was studied. Electrolytes, Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$, and Na_2SO_3, were used as co-existing ions. Some of these electrolytes are fully oxidized while others are partly oxidized. The partly oxidized electrolytes were employed to determine the selectivity of ferrate(VI) for the degradation of the target micropollutant. The results are shown in Figs. 5(a) and 5(b) for TOP and EE2, respectively. The presence of fully oxidized electrolytes., NaCl, $NaNO_3$, and Na_2HPO_4, was not affecting significantly the oxidation of TOP and EE2 by ferrate(VI). However, partly oxidized $NaNO_2$ and Na_2SO_3 electrolytes were caused slightly to decrease the decomposition of TOP and EE2 from aqueous solution. These results clearly implied that the presence of NO_2^- and SO_3^{2-} did not affect the degradation of TOP and EE2 by ferrate(VI) to an appreciable extent. Previously, it was reported that the presence of NO_2^- and SO_3^- greatly affected the degradation of a Zn(II)-NTA complex by ferrate(VI) since ferrate(VI) decomposition increased

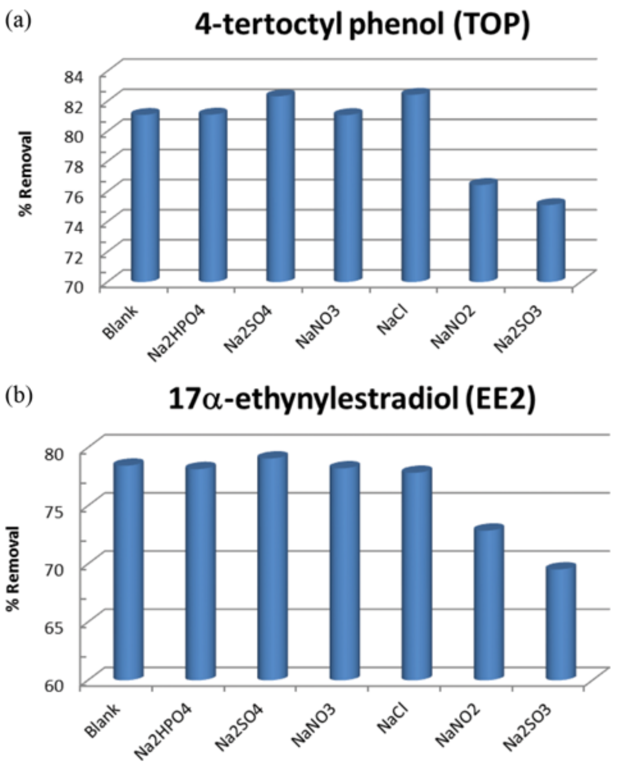

Fig. 5. Effect of background electrolytes on the degradation of (a) TOP; and (b) EE2 by ferrate(VI).

significantly in the presence of these electrolytes [53]. However, these results indicated that $NaNO_2$ and Na_2SO_3 did not affect significantly the degradation of micropollutants by ferrate(VI). To assess further the selectivity of ferrate(VI) towards these partly oxidized electrolytes, the concentration of $NaNO_2$ and Na_2SO_3 was increased from from 0.1 to 5.0 mmol/L at a constant TOP or EE2 concentration and ferrate(VI) concentration of 0.10 mmol/L at pH 8.0. The results are given in Fig. 6. Increasing the background electrolyte concentration from 0.1 to 5.0 mmol/L $NaNO_2$ decreased the percent removal of TOP from 72.87 to 67.23% (i.e., 5.64% only). A similar negligible decrease in percent removal of EE2 was observed in presence of various concentrations of $NaNO_2$. Similarly, a 50-fold (i.e., from 0.1 to 5.0 mmol/L) increase in Na_2SO_3 concentration minimally affected the degradation of TOP or EE2 by ferrate(VI) in aqueous solutions. These results demonstrated the high affinity of ferrate(VI) for the selective degradation of TOP or EE2 from aqueous solution. The ability of ferrate(VI) to degrade TOP and EE2 in aqueous solutions was largely unaffected by the presence of studied co-existing ions.

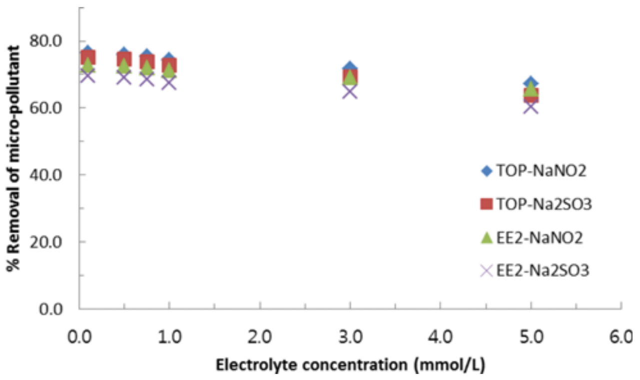

Fig. 6. Effect of various concentrations of background electrolytes on the degradation of TOP and EE2 by ferrate(VI).

CONCLUSIONS

The applicability of ferrate(VI) was assessed for the treatment of aqueous solutions contaminated with the emerging micro-pollutants 4-tert-octylphenol (TOP) and 17α-ethynylestradiol (EE2). Simulated batch reactor operations to assess the degradation of TOP and EE2 from aqueous solutions were performed. The time dependence degradation of TOP and EE2 was assessed as a function of solution pH (7.0 to 12.0) and pollutant concentration, i.e., 0.03 to 0.3 mmol/L at a constant dose of ferrate(VI) (0.10 mmol/L). A decrease in pollutant concentration and pH greatly favored the removal of TOP and EE2 from aqueous solutions. A kinetic study was performed at pH 8.0 and the apparent second-order rate constants were found to be 94.07 and 90.17 L/mol/min, respectively, for the TOP and EE2 molecules. Further, the HPLC data showed that very high percent degradation of TOP and EE2 was achieved using ferrate(VI). Moreover, very high percent removal of EE2 was largely unaffected by an increase in pH from 7.0 to 12.0. A partial but significant percent of TOC was removed by ferrate(VI). Percent TOC removal was increased with decreasing pollutant concentration and pH. However, the percent TOC removal was almost unaffected with the increase in pH from 7.0 to 12.0 by ferrate(VI). The presence of background electrolytes, $NaNO_3$, NaCl, $NaSO_4$ and Na_2HPO_4, was not affecting the degradation of TOP and EE2 by ferrate(VI). Even 50-fold increase of NO_2^- and SO_3^{2-} was not affecting significantly the degradation of TOP and EE2 by ferrate(VI). This highlighted the selectivity of ferrate(VI) towards the TOP and EE2. Overall, the results indicated the potential applicability of ferrate(VI) in a safe and viable treatment of emerging micropollutants from aqueous solutions.

REFERENCES

1. Thanhmingliana, S. M. Lee, D. Tiwari and S. K. Prasad, *RSC Adv.*, **5**, 46834 (2015).
2. S. A. Snyder, P. Westerhoff, Y. Yoon and D. L. Sedlak, *Environ. Eng. Sci.*, **20**, 449 (2003).
3. A. Zafra-Gómez, O. Ballesteros, A. Navalón and J. L. Vílchez, *Microchem. J.*, **88**, 87 (2008).
4. Q. Zhao, Q. Wang, D. Wu, X. Fu, T. Jiang and H. Yin, *J. Ind. Eng. Chem.*, **18**, 1326 (2012).
5. J. Niu, S. Ding, L. Zhang, J. Zhao and C. Feng, *Chemosphere*, **93**, 1 (2013).
6. S. Larcher and V. Yargeau, *Environ. Pollut.*, **173**, 17 (2013).
7. N. Nowotny, B. Epp, C. von Sonntag and H. Fahlenkamp, *Environ. Sci. Technol.*, **41**, 2050 (2007).
8. N. Nakada, H. Shinohara, A. Murata, K. Kiri, S. Managaki, N. Sato and H. Takada, *Water Res.*, **41**, 4373 (2007).

9. B. Yang, G.-G. Ying, J.-L. Zhao, S. Liu, L.-J. Zhou and F. Chen, *Wat. Res.*, **46**, 2194 (2012).
10. M. Aoki, M. Kurasaki, T. Saito, S. Seki, T. Hosokawa, Y. Takahashi, H. Fujita and T. Iwakura, *Life Sci.*, **74**, 2301 (2004).
11. M. Hawrelak, E. Bennett and C. Metcalfe, *Chemosphere*, **39**, 745 (1999).
12. S. Yamazaki, T. Mori, T. Katou, M. Sugihara, A. Saeki and T. Tanimura, *J. Photochem. Photobiol. A: Chem.*, **199**, 330 (2008).
13. R. White, S. Jobling, S. A. Hoare, J. P. Sumpter and M. G. Parker, *Endocrinology*, **135**, 175 (1994).
14. H. I. Kwak, M. O. Bae, M. H. Lee, Y. S. Lee, B. J. Lee, K. S. Kang, C. H. Chae, H. J. Sung, J. S. Shin, J. H. Kim, W. C. Mar, Y. Y. Sheen and M. H. Cho, *Environ. Toxicol. Chem.*, **20**, 787 (2001).
15. J. J. Lech, S. K. Lewis and L. Ren, *Fundamental Appl. Toxicol.*, **30**, 229 (1996).
16. X. Yang, M. Liu, Z. Wang, Q. Li and Z. Zhang, *J. Environ. Sci.*, **25**, 1712 (2013).
17. J. L. Zhou, *Environ. Sci. Technol.*, **40**, 2225 (2006).
18. A. M. R. Ferreira-Leach and E. M. Hill, *Marine Environ. Res.*, **51**, 75 (2001).
19. R. Gadzala-Kopciuch, A. Filipiak and B. Buszewski, *Talanta*, **74**, 655 (2008).
20. S. A. Snyder, T. L. Keith, D. A. Verbrugge, E. M. Snyder, T. S. Gross, K. Kannan and J. P. Giesy, *Environ. Sci. Technol.*, **33**, 2814 (1999).
21. C. Li, X. Z. Li, N. Graham and N. Y. Gao, *Wat. Res.*, **42**, 109 (2008).
22. USFDA, U.S. Food and Drug Administration (USFDA) and National Center for Toxicological Research (NCTR), Endocrine Disruptor Knowledge Base (EDKB), (2012), http://www.fda.gov/scienceresearch/bioinformaticstools/endocrinedisruptorknowledgebase/default.htm.
23. D. Tiwari, J.-K. Yang and S. M. Lee, *Env. Eng. Res.*, **10**, 269 (2005).
24. L. Pachuau, S. M. Lee and D. Tiwari, *Chem. Eng. J.*, **230**, 141 (2013).
25. J. Q. Jiang, *J. Hazard. Mater.*, **146**, 617 (2007).
26. V. K. Sharma, *Adv. Environ. Res.*, **6**, 143 (2002).
27. N. Graham, C.-C. Jiang, X.-Z. Li, J.-Q. Jiang and J. Ma, *Chemosphere*, **56**, 949 (2004).
28. D. Tiwari, L. Sailo and L. Pachuau, *Sep. Purif. Technol.*, **132**, 77 (2014).
29. J. Q. Jiang, *J. Hazard. Mater.*, **146**, 617 (2007).
30. D. Tiwari, H.-U. Kim, B.-J. Choi, S.-M. Lee, O.-H. Kwon, K.-M. Choi and J.-K. Yang, *J. Environ. Sci. Health Part A*, **42**, 803 (2007).
31. Y. H. Lee, J. Yoon and U. V. Gunten, *Environ. Sci. Technol.*, **39**, 8978 (2005).
32. J. Q. Jiang, Q. Yin, J. L. Zhou and P. Pearce, *Chemosphere*, **61**, 544 (2005).
33. D. Tiwari, C. Lalhriatpuia and S.-M. Lee, *J. Ind. Eng. Chem.*, **30**, 167 (2015).
34. C. Li, X. Z. Li, N. Graham and N. Y. Gao, *Wat. Res.*, **42**, 109 (2008).
35. P. Zhang, G. Zhang, J. Dong, M. Fan and G. Zeng, *Sep. Purif. Technol.*, **84**, 46 (2012).
36. V. K. Sharma, S. K. Mishra and A. K. Ray, *Chemosphere*, **62**, 128 (2006).
37. V. K. Sharma, G. W. L. Ill and F. J. Millero, *Chemosphere*, **82**, 1083 (2011).
38. G. A. K. Anquandah, V. K. Sharma, V. R. Panditi, P. R. Gardinali, H. Kim and M. A. Oturan, *Chemosphere*, **91**, 105 (2013).
39. B. Yang, G.-G. Ying, L.-J. Zhang, L.-J. Zhou, S. Liu and Y.-X. Fang, *Wat. Res.*, **45**, 2261 (2011).
40. J.-Q. Jiang, Z. Zhou and O. Pahl, *Sep. Purif. Technol.*, **88**, 95 (2012).
41. Z. Zhang, Y. Feng, Y. Liu, Q. Sun, P. Gao and N. Ren, *J. Hazard. Mater.*, **181**, 1127 (2010).
42. Environment Agency UK: Environmental Risk Evaluation Report: 4-tert-octylphenol (2005).
43. MITI-List: Biodegradation and Bioaccumulation of Existing Chemical Substances under the Chemical Substance Control Law. National Institute of Technology and Evaluation, Japan (2002).
44. J. F. García-Araya, F. Beltrán and A. Aguinaco, *J. Chem. Technol. Biotechnol.*, **85**, 798 (2010).
45. V. K. Sharma, R. Zboril and R. S. Varma, *Acc. Chem. Res.*, **48**, 182 (2015).
46. V. K. Sharma, L. Chen and R. Zboril, *ACS Sustain. Chem. Eng.*, **4**, 18 (2016).
47. J. D. Rush, Z. Zhao and B. H. J. Bielski, *Free Rad. Res.*, **24**, 187 (1996).
48. T. Ohta, T. Kamachi, Y. Shiota and K. Yoshizawa, *J. Org. Chem.*, **66**, 4122 (2001).
49. V. K. Sharma, D. B. O'Connor and D. Cabelli, *Inorg. Chim. Acta*, **357**, 4587 (2004).
50. V. K. Sharma, S. K. Mishra and N. Nesnas, *Environ. Sci. Technol.*, **40**, 7222 (2006).
51. T. Kamachi, N. Nakayama and K. Yoshizawa, *Bull. Chem. Soc. Japan*, **81**, 1212 (2008).
52. N. Noorhasan, B. Patel and V. K. Sharma, *Wat. Res.*, **44**, 927 (2010).
53. J. Yang, D. Tiwari, M. Yu, L. Pachuau, W. Kim and S. Lee, *Environ. Technol.*, **31**, 791 (2010).