CHAPTER 4

CONCLUSIONS
Ferrate(VI) in the form of potassium ferrate (K$_2$FeO$_4$) was synthesized in the laboratory by wet oxidation method. The purity of the synthesized ferrate(VI) was determined with the help of UV-Visible spectrophotometer at the wavelength of 510 nm and was found to be above 95%. The highly reactive ferrate(VI) was fully employed to assess its efficiency towards the treatment several micro-pollutants in particular the degradation of endocrine disrupting chemicals (EDCs) viz., bisphenol A (BPA), diclofenac sodium salt (DFS), 17α-ethynylestradiol (EE2), 4-tert-octylphenol and potassium phthalate from aqueous solutions. The batch reactor operations were performed for various parametric studies in order to assess the suitability/efficiency of ferrate(VI) along with to deduce a plausible mechanism involved in the oxidative degradation of these EDCs. The EDCs were treated at a wide range of pH i.e., from pH 7.0 to 12.0 and at varied concentration of EDCs from 0.03 mmol/L to 0.5 mmol/L using a constant dose of ferrate(VI) i.e., 0.1 mmol/L. The kinetics of ferrate(VI) reduction was conducted in order to reveal the stoichiometry of EDCs with ferrate(VI). It was observed that a 2:1 molar stoichiometry with ferrate to EDCs was obtained in the oxidative degradation of these EDCs by ferrate(VI). It was further evaluated the $k_{app}$ (overall rate constant) values in the oxidation of EDCs was evaluated and was found to be in the order of bisphenol A > EE2 > 4-tert-octylphenol > diclofenac sodium salt > potassium phthalate at pH 7.0. Generally, it was observed that the reactivity of ferrate(VI) was highly pH dependent towards the degradation of EDCs. It was observed from the UV-Visible analytical data that there was a fast degradation at low pH and the rate of degradation was also increased with the increase in EDCs concentrations. The time dependence data showed that a major extent of EDCs were degraded within just $ca$ 10 mins of contact time indicated an extremely high efficiency of ferrate(VI) towards these EDCs.

Further, the ferrate(VI) treated samples of EDCs were subjected for the measurement of pollutant concentration using the HPLC measurements. The data was presented in terms of
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percent removal of EDCs as a function of pH (i.e., pH 7.0 to 12.0) and concentrations of EDCs from 0.03 to 0.5 mmol/L at a constant dose of ferrate(VI) 0.1 mmol/L. The results indicated that a higher percent removal of organic species was observed at lower concentrations of the of EDCs for all the systems studied. It was also observed that at pH 7.0, in Fe(VI) : EDCs molar ratio 1:1, the percent removal was found that 88.6% of bisphenol A, 41.0% of diclofenac sodium salt, 78.13% of 17α-ethynylestradiol (EE2), 83.84% of 4-tert-octylphenol and 51.16% of potassium phthalate, respectively. This followed the degradation of bisphenol A > 4-tert-octylphenol > EE2 > potassium phthalate > diclofenac sodium salt. At pH 7.0, in Fe(VI) : EDCs molar ratio 1:0.3, the pollutants viz., bisphenol A, 17α-ethynylestradiol (EE2) and 4-tert-octylphenol were almost completely removed. The potassium phthalate was degraded to 76.13% and in the diclofenac sodium salt was degraded to 65.0%.

The mineralization of ferrate(VI) treated EDCs samples was obtained with the help of total organic carbon (TOC) analysis. This could apparently enables to estimate the mineralization of these EDCs using a single dose of ferrate(VI). Results showed that a partial but significant amount of the EDCs were mineralized even with the single dose of ferrate(VI). It was found that 45.12% of bisphenol A (BPA), 38.25% of diclofenac sodium salt (DFS), 43.15% of 17α-ethynylestradiol (EE2), 75.99% of 4-tert-octylphenol and 51.96% of potassium phthalate was mineralized for the molar ratio of Fe(VI) : EDCs as 1:0.3 at pH 7.0. Therefore, the degree of TOC percent removal followed the order of 4-tert-octylphenol > potassium phthalate > bisphenol A > 17α-ethynylestradiol (EE2) > diclofenac sodium salt. The decrease in pH of solution greatly favoured the percent mineralization of these pollutants from aqueous solutions. Therefore, pH 7.0 showed relatively higher percent mineralization of all these pollutants. Ferrate(VI) possessesed higher redox potential at acidic conditions and hence accounted for its enhanced reactivity to degrade the organic impurities at lower pH values. The results are explicitly in conformity with the higher redox potential of ferrate(VI)
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at lower pH values with significant increase in the stability at higher pH values; the redox potential of ferrate(VI) was 2.20 V at pH 1.0 whereas it was only 0.72 V at pH 12.0. Moreover, the protonated ferrate species i.e., HFeO$_4^-$ (HFeO$_4^-$↔H$^+$ + FeO$_4^{2-}$ ; pK$_a^2$=7.3) which was dominant at lower pH values (pH 7.0) possessed with larger spin density than the deprotonated species viz., FeO$_4^{2-}$ caused for increased reactivity of ferrate(VI) at lower pH values.

Further, the effect of ionic strength and background electrolyte concentrations on the removal of these EDCs were studied using the ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na$_2$HPO$_4$, Na$_2$SO$_4$, NaNO$_3$, NaCl, NaNO$_2$ and Na$_2$SO$_3$ were used as co-existing ions. Variety of electrolytes is used having partly or fully oxidized ions. Results indicated that the presence of fully oxidized electrolytes viz., NaCl, NaNO$_3$ and Na$_2$HPO$_4$ could not affect significantly the oxidation of BPA by ferrate(VI). It is to be noted that presence of phosphate and nitrate also caused to increase slightly the degradation of the EDCs. This is due to the fact that ferrate(VI) is relatively stable in the phosphate media forming complexes with Fe(III) otherwise forming precipitates of iron oxide which accelerates the spontaneous fast decomposition of ferrate(VI). However, on the other hand the partly oxidized NaNO$_2$ and Na$_2$SO$_3$ are caused significantly the decrease in the decomposition of EDCs from aqueous solutions. The results inferred that the presence of NO$_2^-$ and SO$_3^{2-}$ affect the degradation of BPA up to some extent by the ferrate(VI). Further, the extent of oxidation of EDCs by the ferrate(VI) was studied increasing the NaNO$_2$ or Na$_2$SO$_3$ concentration from 0.1 to 5.0 mmol/L at constant BPA and ferrate(VI) concentrations of 0.1 mmol/L and at pH 8.0. It was noted that increasing the background concentration from 0.1 to 5.0 mmol/L NaNO$_2$ the corresponding decrease in percent removal of bisphenol A (BPA) was from 55.54 to 50.42 % (i.e., 5.12% only), diclofenac sodium salt (DFS) from 39.06% to 35.95 % (i.e., 3.11% only), 17α-ethynylestradiol (EE2) from 72.87% to 65.67 % (i.e., 7.2% only), 4-tert-octylphenol from 76.45 to 67.23 % (i.e., 9.22% only) and potassium phthalate from 43.02 to 39.96 % (i.e.,
3.06% only), respectively. Similarly, for the similar increase in Na$_2$SO$_3$ background electrolyte concentration from 0.1 to 5.0 mmol/L was caused for insignificant decrease in percent removal of these EDCs from aqueous solutions. Therefore, even in presence of partially oxidized electrolytes *viz.*, NaNO$_2$ and Na$_2$SO$_3$ the degradation of BPA, DCF, EE2, 4-tert-octylphenol and potassium phthalate was almost unaffected by the ferrate(VI) clearly pointed the affinity and potential application of ferrate(VI), at least, in the degradation of studied EDCs from aqueous solutions.

The application of ferrate(VI) in the degradation of persistent micro-pollutants is found to be efficient and effective as studied under the batch reactor operations. Further, the ferrate(VI) treatment is apparently devoid with any toxic by-products, which further indicated that ferrate(VI) is one of the ‘Green Chemical’ and the ferrate(VI) based treatment process is, perhaps, a ‘Green Technology’. The batch reactor input data could be useful to be implemented for the large scale or pilot plant level treatment of the wastewaters contaminated with these potential water pollutants.