CHAPTER 2

METHODOLOGY
2. METHODOLOGY

2.1. Materials and Instrumentations

2.1.1. Chemicals and Apparatus

The chemicals used for the experiments were of AR/GR grade. Bisphenol A (C₁₅H₁₆O₂), diclofenac sodium salt (C₁₄H₁₀C₁₂NNaO₂), 17α-ethynylestradiol (C₂₀H₂₄O₂), 4-tert-octylphenol (C₁₄H₂₂O), potassium phthalate monobasic salt (C₈H₈KO₄), iron(III) nitrate nonahydrate (Fe(NO₃)₃₉H₂O) were obtained from Sigma Aldrich Co., USA. Diethyl ether (C₄H₁₀O), hexane (C₆H₁₄), potassium hydroxide (KOH), hydrochloric acid (HCl), sodium hydroxide (NaOH), phosphoric acid (H₃PO₄), disodium hydrogen phosphate (Na₂HPO₄), acetic acid (CH₃COOH), HPLC Water, acetonitrile HPLC grade (CH₃CN), methanol HPLC grade (CH₃OH) were obtained from Merck India Ltd., India. Moreover, the disodium tetraborate decahydrate (Na₂B₄O₇·10H₂O) was obtained from Himedia, India Ltd., India. Purified sodium hypochlorite (NaClO) was obtained from Palanad Enterprises, Nagpur, India. Purified water (18.2 MΩ cm at 25 °C) was obtained from Millipore Water Purification system (Model: Elix 3). This was fully used for the entire solution preparations and other analytical studies.

Glass Filtration System with fritted funnel (10-15µ) was obtained from Merck, India Ltd. and Whatman Filter Paper (GF/A & GF/C grade, 47mm) were used for filtration during Ferrate(VI) preparation. Syringe filter of 25 mm diameter in size and porosity of 0.47 μm was obtained from Whatman, USA which was used for treated samples filtration. Electronic balance (Sartorius, BSA 224S-CW) was used for taking weights of the chemicals. A pH-meter having glass and calomel electrode assembly (Thermo Scientific, Sn B43460) was used for entire pH measurements in aqueous solutions. Before using the pH meter, it was calibrated with the standard buffer solutions.
2.1.2. Reagents

i. Sample Stock solutions: 1.5 mmol/L solution of different EDCs were prepared in purified water.

ii. Standard buffers (pH 4.01, 7.00 & 12.45) were used for calibrating pH meter.

iii. 0.1 mol/L HCl and/or NaOH solutions were employed for adjusting the pH of the sample solutions or otherwise phosphate buffer was used.

iv. Phosphate buffer: 0.001 mol/L of Na$_2$B$_4$O$_7$.10H$_2$O and 0.005 mol/L of Na$_2$HPO$_4$ were mixed and dissolve in a purified water.

2.1.3. Ultra Violet-Visible (UV-Vis) spectrophotometer

The UV-Visible Spectrophotometer (Thermo Electron Corporation, England; Model: Thermo Spectronic UVI) was used to measure the absorbance at specified wavelength of solutions containing ferrate(VI) so as to obtain the concentration of ferrate(VI). Electronic Spectroscopy involves the promotion of electrons from the ground state to the higher energy states. The amount of light absorbed by the sample is as a function of the wavelength (nm unit) is called the absorption spectrum which generally consists of absorption bands. For visible and ultra violet spectrum, electronic excitation occurs in the range 200-800 nm and involves the promotion of electrons to the higher energy molecular orbital. The spectrum consists of a sharp peaks and each peak will correspond to the promotion of electron from one electronic level to another. But, actually sharp peaks are seldom observed and instead, broad absorption bands are recorded. It is due to the fact that the excitation of electrons are also accompanied by the constant vibratory and rotator motion of the molecules (Hollas, 2005). Since the energy levels of a molecule are quantized, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. The concentration of an analyte in solution can be determined measuring the absorbance at some wavelength and applying the Beer-
Lambert’s law which states that ‘the absorbance of the solution containing light absorbing species at a particular wavelength is directly proportional to the concentration of the solution into path length of the sample cell (cm)’.

The principle of this technique lies to the fact that molecules containing $\pi$-electrons or non-bonding electrons ($\sigma$-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals (Mehta, 2011). The more easily excited the electrons (i.e., lower energy gap between the HOMO and the LUMO) the longer the wavelength of light it can absorb.

A spectrophotometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus, the instrument compares the intensity of the transmitted light with that of the incident light. The modern ultra-violet-visible spectrometers consist of light source, monochromator, detector, amplifier and the recording devices. The most suitable sources of light are: tungsten filament lamp and hydrogen-deuterium discharge lamp which is rich in red radiations. Most spectrophotometers are double beam instruments. The primary source of light is divided into two beams of equal intensity. Before dividing it into two beams, the incident radiation is dispersed with the help of a rotating prism and then selected by slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slits for recording purposes. The selected beam is monochromatic which is then divided into two beams of equal intensity. Dispersion grating can also be employed to obtain monochromatic beam of light from the polychromatic radiation. As the dispersion of a single beam or grating is very small, it is not possible to isolate or collimate very narrow band widths. Thus, light from the first dispersion is passed through a slit and then sent to the second dispersion. After the second dispersion, light passes through the exit slit. The main advantage of the second
dispersion is that the band width of the emitted light increases and the light passing through
the exit slit is almost monochromatic. Almost the entire of the stray light is suppressed.

2.1.4. Total Organic Carbon Analyser (TOCA)

The TOC analyzer (Shimadzu, Japan; Model: TOC-VCPH/CPN) was fully employed to
obtain the total organic carbon content data for the study of the degradation of organic
compounds present in water.

A total organic carbon analyzer (TOCA) is an analytical instrument used for
evaluating the total organic carbon content in water samples and may be considered as an
advanced version and an extension of chemical treatments such as of biochemical oxygen
demand (BOD) and chemical oxygen demand (COD). A typical analysis for TOC measures
both the total carbon (TC) present and the inorganic carbon (IC), the latter representing the
content of dissolved carbon dioxide and carbonic acid salts. Subtracting the inorganic carbon
from the total carbon yields TOC (TOC=TC–IC).

The organic carbon is further categorized as purgeable organic carbon (POC) and non-
purgeable organic carbon (NPOC). NPOC is in turn differentiated into, dissolved organic
carbon and particulate organic carbon. Another common variant of TOC analysis involves
removing the IC portion first and then measuring the leftover carbon. This method involves
purging an acidified sample with carbon-free air or nitrogen prior to measurement, and so is
more accurately called non-purgeable organic carbon (NPOC) (Clescerl et al., 1999).

There are two types of TOC measurement methods, one is the differential method and
the other is the direct method. In the differential method both total carbon (TC) and inorganic
carbon (IC) may be determined separately by measuring them independently. Further, the
total organic carbon (TOC) is calculated by subtracting IC from TC. This method is suitable
for samples in which IC is less than TOC, or at least of similar in size. In the direct method,
first IC is removed from a sample by purging the acidified sample with a purified gas, and
then TOC is determined by means of TC measuring method as TC equal to TOC. This method is also called as non-purgeable organic carbon (NPOC) due to the fact that purgeable organic carbon (POC) such as benzene, toluene, cyclohexane and chloroform may be partly removed from a sample by gas stripping. The direct method is suitable for surface water, ground water and drinking water because of, in most cases, less TOC comparing with IC and negligible amount of POC is present in these samples.

Whether the analysis of TOC is by TC-IC or NPOC methods, it may be broken into three main stages, viz., acidification, oxidation and detection and quantification. The first stage, that is, addition of acid and inert-gas sparging allows all bicarbonate and carbonate ions to be converted into carbon dioxide, and this IC product vented along with any POC that was present. The release of these gases to the detector for measurement or to the air is dependent upon which type of analysis is of interest, the former for TC-IC and the latter for TOC (NPOC). The second stage is the oxidation of the carbon in the remaining sample in the form of carbon dioxide (CO$_2$) and other gases. Modern TOC analyzers perform this oxidation step by high temperature oxidation by combustion technique and low-temperature oxidation by employing chemical oxidation (ultraviolet irradiation, heated persulfate, persulfate and UV irradiation combination). Accurate detection and quantification are the most vital components of the TOC analysis process. Conductivity and non-dispersive infrared (NDIR) are the two common detection methods used in modern TOC analyzers. There are some standardized oxidation and detection techniques used in the TOC analyzers and the combination of a specific oxidation and detection method for deriving specific analytical performance range of values is based on some factors like the nature of application or the nature of liquid being tested, and the need which prompted the evaluation.

The TOC analyzer (Shimadzu, Japan; Model : TOC-V$_{\text{CPH/CPN}}$) employed for the present investigation is based on 680°C combustion catalytic oxidation/NDIR method, developed by Shimadzu and the model is highly sensitive, capable of measuring parameters
such as TC, IC, TOC, NPOC with measuring range and detection limit as TC:0 to 25000 and IC:0 to 30000 and 4 µg/L, respectively. The 680°C combustion catalytic oxidation method achieves total combustion of samples by heating them at 680°C in an oxygen-rich environment and the TC combustion tube is filled with a platinum catalyst. Since this utilizes the simple principle of oxidation through heating and combustion, pre treatment and post treatment using oxidizing agents are unnecessary, which enhances operability. The carbon dioxide generated by oxidation is detected using a non-dispersive infrared gas analyzer (NDIR). By adopting a newly designed, high sensitivity NDIR, the TOC-L series achieves high detection sensitivity, with detection limit of 4μg/L, the highest level for the combustion catalytic oxidation method. The sample is delivered to the combustion furnace, which is supplied with purified air. There, it undergoes combustion through heating to 680°C with a platinum catalyst. It decomposes and is converted to carbon dioxide. The carbon dioxide generated is cooled and dehumidified, and then detected by the NDIR. The concentration of total carbon (TC) in the sample is obtained through comparison with a calibration curve formula. Furthermore, by subjecting the oxidized sample to the sparging process, the inorganic carbon (IC) in the sample is converted to carbon dioxide, and the IC concentration is obtained by detecting this with the NDIR. The TOC concentration is then calculated by subtracting the IC concentration from the obtained TC concentration.

2.1.5. High performance liquid chromatography (HPLC)

The HPLC instrument (Waters, USA; Model: Waters 515 HPLC pump, Waters 2489 UV/Visible detector, C18 5µm (4.6x250 mm column)) was fully employed to obtain the degradation of EDCs present in water. In HPLC, a liquid sample, or a solid sample dissolved in a suitable solvent, is carried through a chromatographic column using a liquid mobile phase. Separation is determined by solute/stationary-phase interactions, including liquid–solid
adsorption, liquid–liquid partitioning, ion exchange and size exclusion, and by solute/mobile-phase interactions. In each case, however, the basic instrumentation is essentially the same.

An HPLC typically includes two columns: an analytical column responsible for the separation and a guard column. The guard column is placed before the analytical column, protecting it from contamination. The most commonly used columns for HPLC are constructed from stainless steel with internal diameters between 2.1 mm and 4.6 mm, and lengths ranging from approximately 30 mm to 300 mm. These columns are packed with 3–10 mm porous silica particles that may have an irregular or spherical shape. Typical column efficiencies are 40,000–60,000 theoretical plates/m. Assuming $V_{\text{max}}/V_{\text{min}}$ is approximately 50, a 25 cm column with 50,000 plates/m has 12,500 theoretical plates and a peak capacity. In liquid–liquid chromatography the stationary phase is a liquid film coated on a packing material consisting of 3–10 μm porous silica particles. The stationary phase may be partially soluble in the mobile phase, causing it to “bleed” from the column over time. To prevent this loss of stationary phase, it is covalently bound to the silica particles. Bonded stationary phases are attached by reacting the silica particles with an organochlorosilane of the general form Si(CH₃)₂RCl, where R is an alkyl or substituted alkyl group.

In reverse-phase chromatography, which is the more commonly encountered form of HPLC, the stationary phase is non polar and the mobile phase is polar. The most common nonpolar stationary phases use an organochlorosilane for which the R group is an $n$-octyl (C₈) or $n$-octyldecyl (C₁₈) hydrocarbon chain. Most reverse phase separations are carried out using a buffered aqueous solution as a polar mobile phase. Because the silica substrate is subject to hydrolysis in basic solutions, the pH of mobile phase must be less than 7.5. The elution order of solutes in HPLC is governed by polarity. In a normal phase separation the least polar solute spends proportionally less time in the polar stationary phase and is the first solute to elute from the column. Retention times are controlled by selecting the mobile phase, with a less polar mobile phase leading to longer retention times. If, for example, a separation is poor
Methodology

because the solutes are eluting too quickly, switching to a less polar mobile phase leads to longer retention times and more opportunity for an acceptable separation. When two solutes are adequately resolved, switching to a more polar mobile phase may provide an acceptable separation with a shorter analysis time. In a reverse phase separation the order of elution is reversed, with the most polar solute being the first to elute. Increasing the polarity of the mobile phase leads to longer retention times, whereas shorter retention times require a mobile phase of lower polarity. When a separation uses a single mobile phase of fixed composition it is called an isocratic elution. It is often difficult, however, to find a single mobile phase composition that is suitable for all solutes. Recalling the general elution problem, a mobile phase that is suitable for early eluting solutes may lead to unacceptably long retention times for later eluting solutes. Optimizing conditions for late eluting solutes, on the other hand, may provide an inadequate separation of early eluting solutes. Changing the composition of mobile phase with time provides a solution to this problem. For a reverse-phase separation the initial mobile-phase composition is relatively polar. As the separation progresses, the mobile phase’s composition is made less polar. Such separations are called gradient elutions. The typical operating pressure of an HPLC is sufficiently high that it is impossible to inject the sample in the same manner as in gas chromatography. Instead, the sample is introduced using a loop injector. Sampling loops are interchangeable and available with volumes ranging from 0.5 mL to 2 mL. In the load position the sampling loop is isolated from the mobile phase and is open to the atmosphere. A syringe with a capacity several times that of the sampling loop is used to place the sample in the loop. Any extra sample beyond that needed to fill the sample loop exits through the waste line. After loading the sample, the injector is turned to the inject position. In this position the mobile phase is directed through the sampling loop, and the sample is swept onto the column. After that the UV detector will detect at a particular wavelength which corresponds to each compounds.
2.2. Analytical methods

2.2.1. Preparation of ferrate(VI)

Ferrate(VI) as potassium ferrate (K$_2$FeO$_4$) was prepared adopting the wet chemical oxidation method, with some modifications as described elsewhere (Li *et al*., 2005; Tiwari *et al*., 2007). The Fe(III) was oxidized into ferrate(VI) using the sodium hypochlorite (12-14%). The detailed preparation process is described as: 300 mL of chilled NaClO solution was taken in a beaker and 90g of solid KOH was added slowly in this solution and the resulting suspension was again cooled. The precipitate formed was filtered with GF/C filter paper, to give a clear yellow and highly alkaline NaClO solution. The solution was chilled and filtered using a GF/C filter paper to remove any precipitates occurred from the solution. To this solution, 20g of pulverized ferric nitrate was added slowly within Ca. 2 hours, with constant and vigorous stirring under cold conditions (< 8º C). Further, after the complete addition of the ferric nitrate, the solution was stirred for another Ca. 30 minutes. It was noted that the cold and highly alkaline conditions favored the oxidation of Fe(III) to ferrate(VI). Also the time allowed for stirring may result to achieve an enhanced yield. The color of the solution readily changed yellow brown to purple colour which showed the formation of ferrate(VI).

Further, Ca. 50g of solid KOH was added slowly; with maintaining the solution temperature ≤ 15º C. The solution mixture was allowed to cool standing in a refrigerator for Ca. 40 minutes. The resulting dark purple slurry was filtered with a glass filter (medium porosity 10-15µm) and the filtrate was discarded. The precipitate was washed with cold 3M KOH solution (Ca. 100 mL (20 mL×5). The filtrate from the washings was collected; taken into a flask and Ca. 100 mL of saturated chilled KOH solution was added. The potassium ferrate readily precipitated which was filtered again with a GF/C filter paper. The filtrate was discarded, and the solid was washed with cold 3M KOH solution (Ca. 50 mL) and again the filtrate was collected in a beaker. Similarly, re-precipitation was carried out at least for another 3 times to remove any impurities, if present, hence to enhance the purity of ferrate(VI). Finally, the solid
was flushed with n-hexane (four times × 10 mL) and diethyl ether (two times × 10 mL). The final product was collected carefully, it was almost black in color and stored in a vacuum desiccator (figure 2.1) along with KOH pellets.

Figure 2.1. Dark purple solid potassium ferrate (K$_2$FeO$_4$)

2.2.2. Determination of the purity of the prepared ferrate(VI)

The purity of the prepared ferrate(VI) was assessed using UV-Visible measurement since the standard molar extinction coefficient of ferrate(VI) solution was reported to be 1150 M$^{-1}$ cm$^{-1}$ at 510 nm and at pH~9.2 (Lee et al., 2004). Aqueous solution of ferrate(VI) was prepared at pH 9.2 by dissolving 0.0198 g of ferrate(VI) in phosphate buffer (pH~9.2) and making the volume up to 100 mL (1.0 mmol/L). Immediately, the absorbance of the ferrate(VI) solution was measured with the help of UV-Vis Spectrophotometer at 510 nm wavelength which was previously calibrated for zero absorbance using the phosphate buffer (pH~9.2) as blank reagent. The observed absorbance value was used to calculate the concentration of ferrate(VI) using the Beer-Lambert’s law which is represented with the following equation (2.1).

\[ A = \varepsilon . b . C \]  

... (2.1)

where, A = absorbance of the ferrate(VI) solution

\( \varepsilon \) = molar extinction coefficient of ferrate(VI)
Methodology

\[ \text{Purity \% \ of Fe(VI)} = \frac{\text{Obtained conc.}}{\text{Initial conc. taken}} \times 100\% \times \frac{1}{1 \times 10^{-3} \ M} \]

The purity of ferrate(VI) was found to be > 80 \%. Actual amount of ferrate(VI) was always taken, in each experiment, based on the purity percent obtained to compensate for the impurities present.

2.2.3. Degradation of organic species using ferrate(VI) : UV-Visible measurements

The synthesized ferrate(VI) was used to treat different Endocrine disrupting chemicals (EDCs) such as bisphenol A (C_{12}H_{16}O_{2}), diclofenac sodium salt (C_{14}H_{10}C_{12}NNaO_{2}), 17α-ethynylestradiol (C_{20}H_{24}O_{2}), 4-tert-oktyphenol (C_{14}H_{22}O), potassium phthalate monobasic salt (C_{8}H_{8}KO_{4}). The degradation of these organic species in the presence of ferrate(VI) was observed indirectly by monitoring the change in the concentration of ferrate(VI) with the help of UV-Visible spectrophotometer.

Stock solutions of each EDCs were prepared separately dissolving an appropriate amount of EDCs in milli Q water. The required concentration of EDC was obtained by the successive dilution of stock solutions. And the required pH was adjusted with the drop-wise addition of hydrochloric acid or sodium hydroxide solutions. Batch experiments were performed separately for each Endocrine disrupting chemicals and the degradation of organic species by ferrate(VI) was studied as a function of different pH (i.e., pH 7.0, 8.0, 9.0, 10.0, 11.0, 12.0), molar concentrations of EDCs (0.03 mmol/L, 0.05 mmol/L, 0.075 mmol/L, 0.1 mmol/L, 0.3 mmol/L, 0.5 mmol/L) and time (20 minutes) at constant ferrate(VI) dose (0.1 mmol/L). Before recording absorbance of the sample solution, the UV-Visible Spectrophotomer was always calibrated using the aqueous solution prepared. A known
amount of ferrate(VI) was then added to the EDCs solution such that the resulting solution was having molar concentration of ferrate(VI) to 0.1 mmol/L. Then, absorbance of the sample solution was immediately recorded at 510 nm using UV-Vis spectrophotometer at regular 1 minute interval of time for 20 minutes. Absorbance for the blank, i.e., ferrate(VI) solution at the same pH (i.e., pH 7.0, 8.0, 9.0, 10.0, 11.0, 12.0) and concentration were also recorded for the same intervals of time and period as to observe the self-decomposition of ferrate(VI) at an identical medium. Further, the absorbance of sample was corrected with the blank data. The recorded absorbance were related to the change in concentration of ferrate(VI) and always necessary corrections were conducted using the blank data obtained at that concentration and medium as well. Similar experiments were performed separately for each EDCs at different pH and concentrations. The UV-Vis data obtained for the degradation of ferrate(VI) were then employed for the kinetic studies i.e., the time dependence data was simulated for the pseudo-first and pseudo-second order rate laws to its standard form.

The samples, once after obtaining the UV-Vis data, were filtered using 0.45 μm syringe filter and separated into two parts subjected for other analysis viz., TOC and HPLC. Always a blank sample was used for required comparison in analysis.

2.2.4. Degradation of organic species using ferrate(VI) : TOC measurements

After completing UV-Visible measurements and filtered with 0.45 μm syringe filter, the study of the degradation level of organic species in the same systems under section 2.2.3 was extended in terms of TOC measurements assessing the total organic carbon content of the sample solutions before and after treatment of ferrate(VI) to correlate with the decomposition percent of the organic impurities. The TOC value for each of the above sample solutions with its corresponding blank solutions i.e., in the absence of ferrate(VI) was measured with the help of TOC analyzer (Shimadzu, TOC-VCPH/CPN). The decrease in TOC value of ferrate(VI)
Methodology

treated samples as compared to blank, indicates the extent of the decomposition of the organic species under study due to ferrate(VI) treatment.

The TOC data was then converted into the percent removal using the initial TOC value of EDCs (blank). The total organic carbon value is an indicative of the mineralization of the EDCs from aqueous solution. Therefore, the percent mineralization of EDCs was obtained and presented as a function of EDCs concentration at studied pH. Moreover, the difference in TOC values i.e., the initial and treated samples was utilized in the calculation of percent of EDCs removed and presented as a function of pH and pollutant initial concentrations.

2.2.5. Removal of Endocrine disrupting chemicals: HPLC measurements

The removal of endocrine disrupting chemicals (EDCs) were studied using the HPLC data employing the HPLC instrument (Waters, USA; Model : Waters 515 HPLC pump, Waters 2489 UV/Visible detector, C18 5μm (4.6x250 mm column)). The instrument was calibrated by the standard solutions of different concentrations of each EDCs which were dissolved in HPLC grade water (Merck, India) and the calibration curve was plotted and the $R^2$ values was found almost equal to 1. The blank solutions i.e., in the absence of ferrate(VI) of each EDCs and ferrate(VI) treated samples was analysed to obtain the removal of the EDCs. The parameters used in the HPLC measurements of each EDCs are as followed:

<table>
<thead>
<tr>
<th>Name of EDCs</th>
<th>Mobile phase</th>
<th>Wavelength (nm)</th>
<th>Injection volume (μL)</th>
<th>Flow rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A (BPA)</td>
<td>Acetonitrile : water (70 : 30)</td>
<td>276</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>Diclofenac sodium salt (DFS)</td>
<td>Acetonitrile : water : acetic acid (70 : 29 : 1)</td>
<td>276</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>17α-ethynylestradiol (EE2)</td>
<td>Acetonitrile : water : acetic acid (70 : 29 : 1)</td>
<td>280</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>4-tert-octylphenol</td>
<td>Acetonitrile : water (70 : 30)</td>
<td>222</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Potassium phthalate</td>
<td>Acetonitrile : water (70 : 30)</td>
<td>230</td>
<td>20</td>
<td>1</td>
</tr>
</tbody>
</table>
The peak formed at a particular retention time was corresponded to a particular EDC and it was directly proportional to the concentration of analyte. The peak area was calculated using a software Empower2 and for the estimation of concentration of that EDC. The area of peak calculation was used to obtain the percent removal of EDCs. The results were then presented as percent of EDC removed as a function of EDC concentration and pH. The decrease in pollutant EDCs value of ferrate(VI) treated samples as compared to blank, indicated the extent of degradation of the pollutant under study due to ferrate(VI) treatment.

2.2.6. Effect of background electrolytes and ionic strength

The effect of background electrolytes on the reduction efficiency of ferrate(VI) in presence of different EDCs were investigated using six different types of electrolytes, viz., Na₂HPO₄, Na₂SO₄, NaNO₃, NaCl, NaNO₂ and Na₂SO₃. A sample solution of EDCs (0.1 mmol/L) was prepared and to it, a known amount of electrolyte was added such that the resulting solution contains molar ratios of EDCs to electrolyte as 1:1. Using drops of dilute HCl/NaOH, the solution was adjusted to pH 8.0. Then, a known amount of ferrate(VI) was added so as to achieve the concentration of ferrate(VI) as 0.1 mmol/L, i.e., the stoichiometric ratios of 1:1:1 for EDCs, electrolyte and ferrate(VI). The change in concentration of ferrate(VI) in the solution was observed recording the absorbance of the solution at the wavelength of 510 nm using UV-Visible spectrophotometer at regular time interval for a specified period. Similarly, absorbance of blank solution, i.e., in absence of EDCs and electrolyte was also recorded for comparison and necessary correction, if needed. The solutions were stirred for 2 hrs and then filtered using the syringe filter (0.45 μm) and divided into two parts and one part was subjected for the measurement of EDCs concentrations using the HPLC and another part was subjected for the total mineralisation of EDCs using the TOC analyser.
In order to further investigate the effect of ionic strength on the degradation efficiency of EDCs by the ferrate(VI), two electrolytes NaNO_2 and Na_2SO_3 were selected. The electrolyte concentrations i.e., 0.01, 0.05, 0.075, 0.1, 0.3 and 0.5 mmol was prepared in the phosphate buffer at pH 8.0 and then the solutions were used for the preparation of EDCs 0.1 mmol/L. Then a known amount of ferrate(VI) was added to achieve the ferrate dose of 0.1 mmol/L was added to the solutions. The change in concentration of ferrate(VI) as a function of time was checked with the help of UV-Visible spectrophotometer (Thermo, UV1). The same experiment was repeated for remaining solutions containing different electrolyte concentrations. The change in total EDCs concentration was checked after filtration of ferrate(VI) treated samples using 0.45 µm syringe filter and was analyzed using an HPLC instrument (Waters, USA; Model : Waters 515 HPLC pump, Waters 2489 UV/Visible detector, C18 5µm (4.6x250 mm column)). Also the mineralisation of EDCs was measured by TOC analyzer (Shimadzu, TOC-VCPH/CPN).