CHAPTER 3

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3.1. Materials

3.1.1. Chemicals and Apparatus

The chemicals used for the experiments were of AR/GR grade. Iminodiaecetic acid (C_{4}H_{7}NO_{4}), nitrilotriacetic acid (C_{6}H_{9}NO_{6}), iron(III) nitrate nanohydrate (Fe(NO_{3})_{3}.9H_{2}O), diethyl ether (C_{4}H_{10}O), hexane, (C_{6}H_{14}) were obtained from Sigma Aldrich Co., USA. potassium hydroxide (KOH), nickel(II) sulphate heptahydrate (NiSO_{4}.xH_{2}O), zinc chloride (ZnCl_{2}), copper sulphate pentahydrate (CuSO_{4}.5H_{2}O), hydrochloric acid (HCl), sodium chloride (NaCl), sodium nitrite (NaNO_{2}), sodium nitrate (NaNO_{3}), sodium sulphite (Na_{2}SO_{3}), sodium sulphate (Na_{2}SO_{4}), sodium phosphate (Na_{3}PO_{4}), phosphoric acid (H_{3}PO_{4}) were obtained from Merck India Ltd., India. Disodium ethylenediamine tetraacetic acid (C_{10}H_{14}N_{2}Na_{2}O_{8}.2H_{2}O), cadmium nitrate (Cd(NO_{3})_{2}.4H_{2}O) was procured from the Loba Chemie, India. Moreover, the disodium tetraborate decahydrate (Na_{2}B_{4}O_{7}.10H_{2}O), disodium hydrogen phosphate (Na_{2}HPO_{4}) was obtained from Himedia, India Ltd., India. Purified sodium hypochlorite (NaClO) was obtained from Palanad Enterprises, Nagpur, India. Purified water (10-15 MΩ cm), obtained from Millipore Water Purification system (Model: Elix 3) was used for entire solution preparations and other analytical studies. Standard solutions of copper, zinc, cadmium and nickel (1000 ppm) were obtained from Merck. These solutions were diluted and used for calibration of AAS.

Glass Filtration System with fritted funnel (10-15µ) obtained from Merck, India Ltd. and Whatman Filter Paper (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 m 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
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Ferrate(VI) in wastewater treatment glass and calomel electrode assembly (EUTECH Instruments; Model: Cyberscan pH 310, pH/MV/°C/°F Data meter) was used for entire pH measurements in aqueous solutions. Before using the pH meter, it was calibrated with the known buffer solutions.

3.1.2. Reagents

i. Sample Stock solutions: 0.01M solution of different metal complexes.

ii. Standard Buffers (pH 4.01, 7.00 & 12.45) for calibrating pH meter.

iii. HNO₃ and NaOH for adjusting pH of the sample solutions.

3.1.3. Ultra violet-Visible (UV-Vis) spectrophotometer

The UV-Visible Spectrophotometer (Thermo Electron Corporation, England; Model: Thermo Spectronic UVI ) was used to measure the wavelength of solutions containing Fe(VI) so as to obtain the concentration of Fe(VI).

UV-Vis spectrometer was used to measure the absorption of light intensity at particular wavelength of incident light. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels. For visible and ultra violet spectrum, electronic excitation occurs in the range 200-800nm and involves the promotion of electrons to the higher energy molecular orbitals. UV-Vis spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by 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.

The alternative title of this technique is Electronic Spectroscopy since it 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 ultraviolet 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 corresponds 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 rotatory 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.

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.

3.1.4. Atomic Absorption Spectrophotometer (AAS)

Flame A.A.S. (Perkin-Elmer, AAnalyst200) was employed for the quantitative estimation of total metal concentrations, viz., copper, cadmium, zinc and nickel. Flame atomic absorption is a very common technique for detecting metals and metalloids in environmental samples. It is a very convenient, reliable, simple and widespread technique and has an acceptable level of accuracy for most analytes. The technique is based on the fact that ground state metals absorb light at specific wavelengths, as such making use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on Beer-Lambert Law. In short, the electrons of the atoms in the atomizer can
be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. There are no vibration or rotation energy levels that would widen the lines to brands in the spectrum like it happens in the case of UV-Vis spectroscopy. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using Beer-Lambert’s law stating that, “the absorbance of an absorbing analyte is proportional to its concentration”.

In 1955, based on the Kirchoff’s law, "Matter absorbs light at the same wavelength at which it emits light", Walsh suggested the use of cathode lamps to provide an emission of appropriate wavelength (Walsh, 1955); and the use of a flame to produce neutral atoms that would absorb the emission as they crossed its path. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve. The technique of flame atomic absorption spectroscopy (FAAS) requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 °C. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths which are element specific and accurate to 0.01-0.1nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the
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flame. A device such as photon multiplier can detect the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample.

Flame atomic absorption hardware is divided into six fundamental groups that have two major functions: generating atomic signals and signal processing. Signal processing is a growing additional feature to be integrated or externally fitted to the instrument. The instrument parts include a cathode lamp, a stable light source which is necessary to emit the sharp characteristic spectrum of the element to be determined. A different cathode lamp is needed for each element, although there are some lamps that can be used to determine three or four different elements if the cathode contains all of them. Each time a lamp is changed, proper alignment is needed in order to get as much light as possible through the flame, where the analyte is being atomized, and into the monochromator. The atom cell is the part with two major functions: nebulization of sample solution into a fine aerosol solution, and dissociation of the analyte elements into free gaseous ground state form. Not all the analyte goes through the flame, part of it is disposed. As the sample passes through the flame, the beam of light passes through it into the monochromator. The monochromator isolates the specific spectrum line emitted by the light source through spectral dispersion, and focuses it upon a photomultiplier detector, whose function is to convert the light signal into an electrical signal. The processing of electrical signal is fulfilled by a signal amplifier. The signal could be displayed for readout or further fed into a data station for printout by the requested format (Skoog, 1992; Kenkel, 1994).
3.1.5. 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 organics present in water.

A total 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) and 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 TC (Total Carbon) and IC (Inorganic Carbon) may be determined separately by measuring them independently. Further, the TOC (Total Organic Carbon) may be calculated by subtracting IC from TC. This method is suitable for samples in which IC is less than TOC, or at least of similar size. In the direct
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method, first IC is removed from a sample by purging the acidified sample with a purified
gas, and then TOC may be determined by means of TC measuring method as TC equal to
TOC. This method is also called as NPOC (Non-Purgeable Organic Carbon) due to the fact
that POC (Purgeable Organic Carbon) 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 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 in to 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 (CO₂) 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.
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The TOC Analyzer (Shimadzu, Japan; Model: TOC-VCPH/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, pretreatment and post-treatment using oxidizing agents are unnecessary, which enhances operability. The carbon dioxide generated by oxidation is detected using an infrared gas analyzer (NDIR). By adopting a newly-designed, high-sensitivity NDIR, the TOC-L series achieves high detection sensitivity, with detection limit of 4 µg/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 TC (total carbon) in the sample is obtained through comparison with a calibration curve formula. Furthermore, by subjecting the oxidized sample to the sparging process, the IC (inorganic carbon) 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.

3.1.6. Ion Chromatograph

Ion chromatograph (Metrohm, Modular IC System) was employed for the study of the decomplexation of organometallic complexes.
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The term 'ion chromatography' was coined in 1975 with the introduction of detection by conductivity combined with a chemical reduction in conductivity by Small, Stevens and Baumann; it was subsequently used as a trade name for marketing purposes for a long time. In the meantime the abbreviated term 'ion chromatography' has become established as the super ordinate term for the ion exchange, ion exclusion and ion pair chromatography methods included under high performance liquid chromatography (HPLC) (Small et al., 1975). Ion chromatography includes all rapid liquid chromatographic separations of ions in columns coupled online with detection and quantification in a flow-through detector.

IC today is dominant in the determination of anions while the atomic spectrometry methods, commonly used for the determination of cations, are hardly useful for determining the electronegative anion formers of the fifth to seventh main groups of the periodic system. The most important field of application today for anion chromatography is the routine investigation of aqueous systems; this is of vital importance in the analysis of drinking water (Harmet et al., 1998; Haddad and Jackson, 1990). IC is also used for the analysis of the element species in anionic elements or complexes; this is mainly for solving environmentally relevant problems. The third largest field of application for anion chromatography is ultra-trace analysis in ultrapure process chemicals required chiefly in the semiconductor industry.

IC allows separation using ion exchange, ion exclusion, or ion-pair approaches. IC separations are based on differences in charge density of the analyte species, which in turn depend on the valence and size of the individual ionic species to be measured. Separations are also performed on the basis of differences in the hydrophobic character of the ionic species. IC is typically performed at ambient temperature. As with other forms of HPLC, IC separations are based on varying capacity factors and typically follow the Knox equation. Ion chromatography is a technique complimentary to the more commonly used reversed-phase
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and normal-phase HPLC and to atomic absorption and ion-coupled plasma (plasma spectro-chemistry) techniques in pharmaceutical analysis.

IC can be classified as a liquid chromatographic method, in which a liquid permeates through a porous solid stationary phase and elutes the solutes into a flow-through detector. The stationary phase is usually in the form of small-diameter (5-10 mm) uniform particles, packed into a cylindrical column. The column is constructed from a rigid material (such as stainless steel or plastic) and is generally 5-30 cm long and the internal diameter is in the range of 4-9 mm. A high pressure pump is required to force the mobile phase through the column at typical flow rates of 1-2 ml/min. The sample to be separated is introduced into the mobile phase by injection device, manual or automatic, prior to the column. The detector usually contains low volume cell through which the mobile phase passes carrying the sample components.

The mechanism of interaction of the solutes with the stationary phase determines the classification of the mode of liquid chromatography. In ion chromatography the basic interaction is ionic. The stationary phase is charged due to fixed anions or cations, which are neutralized by counter ions of the corresponding opposite charge. The counter ions can be exchanged by other ions either from the mobile phase or from the sample, hence the name ion-exchange chromatography.

IC instruments closely resemble conventional HPLC instruments. Typical components include an auto sampler, a high-pressure pump, an injection valve with a sample loop of suitable size (typically 10 to 250 µL), a guard column, an analytical column, an optional suppressor or other forms of a post column reaction system, a flow-through detector, and a data system ranging in complexity from an integrator to a computerized data system.
3.1.7. Inductively Coupled Plasma

ICP-MS (Perkin-Elmer, Optima 2000 DV,) was used for the estimation of metal concentration such as Cu(II) contained in the samples in presence and absence of Fe(VI). Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. An inductively coupled plasma (ICP) is a very high temperature (7000-8000K) excitation source that efficiently desolvates, vaporizes, excites, and ionizes atoms atomic-emission spectroscopy and to ionize atoms for mass spectrometry. In ICP, the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields (Montaser and Golightly, 1992).

Inductively coupled plasma contains a sufficient concentration of ions and electrons to make the gas electrically conductive. The plasmas used in spectrochemical analysis are essentially electrically neutral, with each positive charge on an ion balanced by a free electron (Wikipedia, 2010).

The basic set up of an ICP consists of three concentric tubes, most often made of silica. These tubes, termed outer loop, intermediate loop, and inner loop, collectively make up the torch of the ICP. The torch is situated within a water-cooled coil of a radio frequency (RF) generator. As flowing gases are introduced into the torch, the RF field is activated and the gas in the coil region is made electrically conductive. The system offers extremely high sensitivity for the determination of a wide range of elements at extremely low level.

Often, ICP is used in conjunction with other analytical instruments, such as the Atomic Emission Spectroscopy (AES) and the Mass Spectroscopy (MS). This is an advantageous practice, as both the AES and MS require that sample is to be in an aerosol or gaseous form prior to injection into the instrument. Thus, using an ICP in conjunction with either of these
Instruments eliminates any sample preparation time which would be required in the absence of an ICP.

Inductively coupled plasma mass spectroscopy (ICP-MS) was developed in the late 1980's to combine the easy sample introduction and quick analysis of ICP technology with the accurate and low detection limits of a mass spectrometer. An ICP-MS can be thought of as four main processes, including sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination, and the detection system. The resulting instrument is capable of trace multi-element analysis, often at the part per trillion levels electrically conductive. The ICP-MS instrument employs argon plasma (ICP) as the ionization source and a mass spectrometer (MS), usually with a quadrupole mass filter, to separate the ions produced. It can simultaneously measure most elements in the periodic table and determine analyte concentrations down to the sub nanogram per liter, or parts per trillion (ppt) level. It can perform qualitative, semi quantitative, and quantitative analysis, and compute isotopic ratios on water samples, and in waste extracts and digests. ICP-MS offers detection limits in the attomolar range, regardless of the molecular environment of the target element (Mounicou et al., 2010).

3.2. Analytical Methods

3.2.1. Preparation of Ferrate(VI)

Ferrate(VI) as Potassium ferrate ($K_2FeO_4$) was prepared by adopting wet chemical oxidation method, with some modifications as described elsewhere (Li et al., 2004; Tiwari et al., 2007). The Fe(III) was oxidized into Fe(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 90 g 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 2 hours, with constant and vigorous stirring under cold conditions (< 8° C). Further, after the complete addition of the ferric nitrate, the solution was stirred for another 30 minutes. It was noted that the cold and highly alkaline conditions favored the oxidation of Fe(III) to Fe(VI). Also the time allowed for stirring may result in enhanced yield. The color of the solution readily changed to purple showed the formation of Fe(VI). Further, 50 g of solid KOH was added slowly; with maintaining the solution temperature ≤ 15º C. The solution mixture was allowed to cool by standing in a refrigerator for 40 mins. 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 (100mL, 20mL×5). The filtrate from the washings was collected; taken into a flask and 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 (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 Fe(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 NaOH pellets.
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3.2.2. Determination of the purity of the prepared Fe(VI)

The purity of the prepared Ferrate(VI) was assessed using UV-Visible measurement since the standard molar extinction coefficient of Fe(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 Fe(VI) was prepared at pH 9.2 by dissolving 0.0198 g of Fe(VI) in phosphate buffer (pH-9.2) and making the volume up to 100 mL (1.0 mmol/L). Immediately, the absorbance of the Fe(VI) solution was measured with the help of UV-Vis Spectrophotometer at 510 nm wavelength which was previously calibrated at zero absorbance using the phosphate buffer (pH 9.2) as blank reagent. The observed absorbance value was used to calculate the concentration of Fe(VI) following Beer-Lambert’s law which is represented by the following equation (2.1).

\[
A = \varepsilon \cdot b \cdot c \tag{2.1}
\]

where,
\[A = \text{absorbance of the Fe(VI) solution}\]
\[\varepsilon = \text{molar extinction coefficient of Fe(VI)}\]
\[(1150 \text{ L/mol/cm}) \text{ at 510 nm at pH 9.2)}\]
\[b = \text{length of a quartz cell or path length of light (cm)}\]
\[c = \text{concentration of the soluble Fe(VI) (mol/L)}\]
The purity of Fe(VI) was found to be > 95%. Actual amount of Fe(VI) was always taken, in each experiment, based on the purity percent obtained to compensate for the impurities present.

3.2.3. Degradation of organic species using Fe(VI) / UV-Visible measurements

The synthesized ferrate(VI) was used to treat different organic species such as IDA, EDTA and NTA in single systems and in metal complexed systems. The metal complexes taken for the study include heavy metals such as Cu, Cd, Zn and Ni complexed with IDA, NTA and EDTA. The degradation of the organic species in metal complexes as well as in the single systems in presence of Fe(VI) was observed indirectly by monitoring the change in the concentration of Fe(VI) with the help of UV-Visible spectrophotometer.

Batch experiments were first performed for the single systems. The degradation of organic species in single systems by Fe(VI) was studied as a function of molar concentrations of Fe(VI) and time at different but constant pH values. $2.0 \times 10^{-4}$ mol/L of IDA solution was first prepared using phosphate buffer pH 10. In case any slight change in pH occurred, the solution pH was again adjusted by addition of drops of $H_3PO_4/NaOH$. A known amount of Fe(VI) was then added to this solution such that the resulting solution was having molar concentration of Fe(VI) as $0.5 \times 10^{-4}$ mol/L. Then, absorbance of the sample solution was immediately recorded at 510 nm using UV-Vis spectrophotometer at regular interval of time for 30 minutes. Absorbance for the blank, i.e., Fe(VI) in buffer solution was also recorded for the same intervals of time and period as to observe the self-decomposition of Fe(VI) in the studied medium. Further, the absorbance of sample was corrected with the blank data. Again,
the experiment was repeated increasing the concentration of Fe(VI) from \(0.5 \times 10^{-4}\) mol/L to \(7.0 \times 10^{-4}\) mol/L for the same concentration of IDA i.e., \(2.0 \times 10^{-4}\) mol/L. The recorded absorbance were related to the change in concentration of Fe(VI) and always necessary corrections were conducted using the blank data obtained at that concentration and medium as well. Similar experiments were performed for EDTA system taking molar ratios of EDTA and Fe(VI) as 2:0.5, 2:1, 2:2, 2:3, 2:5, 2:7 wherein the concentration of EDTA remains constant at \(2.0 \times 10^{-4}\) mol/L. Similarly, degradation of NTA in presence of Fe(VI) was studied in various concentrations of Fe(VI) as a function of time at different but constant pH values. Batch experiments were again performed as above by treating \(1.0 \times 10^{-4}\) mol/L of NTA solution with varying doses of Fe(VI), from \(0.5 \times 10^{-4}\) mol/L to \(15.0 \times 10^{-4}\) mol/L.

In case of complex systems, the degradation of organic species/decomplexation of the metal complexes were investigated as a function of molar concentration of the metal complex species and different time intervals keeping constant but different solution pH. Batch experiments were first performed for Cu-IDA system. 0.01 mol/L aqueous stock solution of Cu-IDA was prepared using CuSO\(_4\) salt and IDA which was then diluted and the solution pH 8 was adjusted to 8.0 by the addition of concentrated NaOH (1 mol/L) solution. Further, a series of 100 mL (each) of Cu-IDA solutions having different Cu(II) to IDA molar ratios ranging from 0.5 to 15.0 mmol/L were obtained. The pH of these solutions was again checked and adjusted to pH 8 by drop wise addition of concentrated NaOH. Then, a known quantity of Fe(VI) was carefully weighed and introduced into these sample solutions (the weight of Fe(VI) was taken so as to obtain 1.0 mmol/L of Fe(VI) in the sample solution). The resulting solutions were quickly taken into the UV-Visible spectrophotometer and the absorbance reading at 510 nm was recorded at the interval of 1 min for a period of 20 mins. Similar, observations were obtained for all the samples prepared previously. Absorbance of
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Fe(VI) in blank buffer solution at pH 8 were also recorded for necessary absorbance correction to compensate for self-decomposition of Fe(VI). Before recording absorbance of the sample solution, the UV-Visible Spectrophotomer was always calibrated using the aqueous solution prepared at that pH. The similar experiments were repeated at different pH values, i.e., pH 9.0, 10.0, 11.0, 12.0. Similarly, for other metal complex systems i.e., Cu(II)-NTA, Cu(II)-EDTA, Zn(II)-IDA, Zn(II)-NTA, Zn(II)-EDTA, Ni(II)-IDA, Ni(II)-NTA, Ni(II)-EDTA, Cd(II)-IDA, Cd(II)-NTA and Cd(II)-EDTA were studied for the decomplexation and degradation of organic impurities using a constant dose of Fe(VI). The UV-Vis data obtained for the degradation of Fe(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 (single and complexed systems), once after obtaining the UV-Vis data, were further stirred for 2 hrs and then filtered using 0.45 μm syringe filter and subjected for other analysis viz., TOC and AAS. Always a blank sample was used for required comparison in analysis.

3.2.4. Degradation of organic species using Fe(VI) / TOC measurements

Complementary to the UV-Visible measurements, the study of the degradation level of organic species in the same systems under section 3.2.3 was extended in terms of TOC measurements by assessing the total organic carbon content of the sample solutions before and after treatment with Fe(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 solution i.e., in the absence of Fe (VI) was measured with the help of TOC analyzer (Shimadzu, TOC-VCPH/CPN). The decrease in TOC value indicates the extent of the decomposition of the organic species under study due to Fe(VI) treatment.
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Similarly, the degradation of organics in the complexed systems was obtained using the TOC analysis. The blank solutions were also analyzed for TOC for necessary corrections. Hence, the corrected values inferred to the degradation of NTA in solution.

3.2.5. Removal of metals (AAS/ICP measurements)

The above mentioned complexed samples (vide section 3.2.3) treated with Fe(VI) were further divided into two separate portions. Once portion’s pH was raised to pH 12.0 by the addition of Conc. NaOH (2.0 mol/L) and the other portion was kept at such. Both portions were filtered using 0.45 μm syringe filter and then subjected for its metal concentrations using AAS or ICP analytical methods. The initial concentration of metal(II) was also obtained by employing the blank solutions and analyzed the metal concentrations using AAS/ICPS. The subsequent removal of metal ions through adsorption/coagulation by reduced Fe(III) following the degradation of metal complexes by Fe(VI) is observed by the decrease in concentration of metal concentration in the treated and filtered samples. The calibration of the instrument was always performed with the standard solutions of the metal solutions.

The percent removal of metal ions was calculated using the following equation (2.2).

\[
\% = \left( \frac{[\text{Initial Metal}]}{[\text{Metal of treated sample}]} \right) \times 100 \quad \text{...(2.2)}
\]

where,
- Initial metal concentration
- Metal concentration of treated sample

3.2.6. Study of degradation of M(II)-EDTA complexes using IC measurements

The study of the degradation of metal complexes due to Fe(VI) treatment is extended with direct measurement of the dissociated anions using ion chromatograph (Metrohm Modular IC System).
pH dependence of the decomplexation of Cu(II)-EDTA was also studied with the help of IC measurements. 0.10 mmol/L of Cu(II)-EDTA was treated with 2.4 mmol/L of Fe(VI) at different pH values, for 60 minutes of total reaction time. The ionic strength of the solution was maintained at 0.01 M with NaNO₃. The solution pH was maintained within ±0.1 of the desired value using the 0.01 M NaOH or 0.01 M HNO₃ during the reaction period. Aliquots of the solution were periodically removed from reactors and rapidly filtered through 0.45 μm membrane filters and the change in concentration of Cu(II)-EDTA was checked with the help of ion chromatograph (Metrohm Modular IC System) which was calibrated previously with the known concentrations of Cu(II)-EDTA at the same pH. The results were obtained as a function of time and at different pH values. The IC measurements for other samples were not continued because of the difficulty occurred as the column used to get choked in presence of small sized floc particles of Fe(III).

3.2.7. Effect of background electrolytes and ionic strength

The effect of background electrolytes on the reduction efficiency of Fe(VI) in presence of different metal complexes was investigated using seven different types of electrolytes, viz., NaNO₃, NaNO₂, Na₂SO₃, Na₂SO₄, NaCl, NaClO₄ and Na₃PO₄. A sample solution of metal complex (1x10⁻⁴ mol/L) was prepared using phosphate buffer and to it, a known amount of electrolyte was added such that the resulting solution contains molar ratios of metal complex to electrolyte as 1:1. Using drops of H₃PO₄/NaOH, the solution was adjusted to pH 10.0. Then, a known amount of Fe(VI) was added so as to achieve the concentration of Fe(VI) as 1.0x10⁻⁴ mol/L, i.e., the stoichiometric ratios of 1:1:1 for metal complex, electrolyte and Fe(VI). The change in concentration of Fe(VI) in the solution was observed by 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 metal complex and electrolyte was also recorded for comparison and necessary correction, if needed.

In order to further investigate the effect of ionic strength on the reduction efficiency of Fe(VI) as a function of time, Zn(II)-NTA system was also taken for this study. Zn(II)-NTA solution (1.0x10^{-4} \text{ mol/L}) containing varying concentrations of NaNO_3 ranging from 1.0 mmol/L to 1.0 mol/L were taken in different beakers and the pH of each solution was adjusted to 9.2 by addition of drops of conc. HNO_3/NaOH solutions. Then a known amount of Fe(VI) for achieving ferrate dose of 1.0 \times 10^{-4} \text{ mol/L} was added to the solution. The change in concentration of Fe(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 NaNO_3 concentration. The change in total zinc concentration was checked after filtration of Fe(VI) treated samples using 0.45 \mu m syringe filter and was analyzed by an inductively coupled plasma (Optima 2000 DV, Perkin-Elmer). The degradation of NTA was measured by TOC (total organic carbon) analyzer.