CHAPTER

1

INTRODUCTION
1. INTRODUCTION

Water is a transparent fluid which forms the World's streams, lakes, oceans and rain, and is a major constituent of the fluids of living beings. Water covers *Ca 71%* of the Earth's surface (CIA, 2008). It is, naturally, vital for all known forms of life. On Earth, 96.5% of the planet's water is found in seas and oceans, 1.7% in groundwater, 1.7% in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, and 0.001% in the air as vapor, clouds (formed of ice and liquid water suspended in air), and precipitation (Gleick, 1993; UNEP, 1995). Only 2.5% of the Earth's water is available as freshwater, and 98.8% of that water is in ice (excepting ice in clouds) and groundwater. Less than 0.3% of all freshwater is in rivers, lakes, and the atmosphere, and an even smaller amount of the Earth's freshwater (0.003%) is contained within biological bodies and manufactured products (Gleick, 1993). Water resources are becoming increasingly scarce and needs to be sustained, globally and locally. One of the most serious problems faced by billions of people today is the availability of fresh water. It has been estimated that 1.2 billion people have no water within 400m of their dwelling. Governments and organisations all over the world have realized that sustainable water and wastewater management is a necessary component of functioning communities. Safe drinking water is essential to humans and other life forms even though it provides no calories or organic nutrients. Access of safe drinking water has improved over the last few decades in almost every part of the world, but still approximately one billion people lack of accessing the safe water and over 2.5 billion people lacks with adequate sanitation. There is a clear correlation between access of safe water and gross domestic product per capita.

Hydrologists consider a country to be under water stress when its annual water supplies drop to between 1,000 and 1,700 cubic meters per person. In turn, countries face water scarcity when their annual water supplies drop below 1,000 cubic meters per person. Once a country enters the water-scarce category, it faces severe constraints on food
production, economic development, and protection of natural ecosystems. More and more countries are facing water stress and scarcity as their populations grow, urbanization accelerates induces an increased water consumption. Thirty-one countries (with a combined population of close to half a billion) faced water stress or scarcity as of 1995. The number of people estimated to live in water-short countries increased by nearly 125 million between 1990 and 1995. By 2025, 50 countries and more than 3.3 billion people are likely to face water stress or scarcity. By 2050, the number of countries afflicted with water stress or scarcity will rise to 54, and their populations to 4 billion people—40% of the projected global population of 9.4 billion. (Gardner-Outlaw et al., 1997; UNFPA, 1997). Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70% of the fresh water used by humans goes to agriculture (Baroni et al., 2007). Poor water quality and bad sanitation are deadly; some five million deaths a year are caused by polluted drinking water. Enhanced level of wastewater generated globally contains an endless variety of toxic chemicals and pathogens posing a constant serious threat to the aquatic life, human health and the environment. No doubt the human health risk is a major and most widespread concern linked greatly to water quality. Each year ~3.5 million deaths related to inadequate water supply, sanitation and hygiene occur, predominantly in developing countries (WHO, 2008). Diarrheal diseases, often related to contaminated drinking water, are estimated to cause the death of more than 1.5 million children under the age of five per year (UNICEF/WHO, 2009).

Fresh water is emerging as the most critical resource issue facing humanity. While the supply of fresh water is limited, both the world’s population and demand for the resource continues to expand rapidly. The world’s rapid population growth over the last century has been a major factor in increasing global water usage. But demand for water is also rising because of urbanization, economic development, and improved living standards. Between
1900 and 1995, for example, global water withdrawals increased by over six times—more than double the rate of population growth (Gleick, 1993). In developing countries, water withdrawals are rising more rapidly—by four percent to eight percent a year for the past decade—also because of rapid population growth and increasing demand per capita (Marcoux, 1994). Moreover, increasing pollution is shrinking the supply of fresh water even further. In many countries, lakes and rivers are used as receptacles for an assortment of wastes—including untreated or partially treated municipal sewage, industrial poisons, and harmful chemicals that leach into surface and ground water during agricultural activities. Water, however, is not a finite resource, but rather re-circulated as potable water in precipitation in quantities many degrees of magnitude higher than human consumption. Therefore, it is the relatively small quantity of water in reserve in the earth (about 1% of our drinking water supply, which is replenished in aquifers around every 1 to 10 years), that is a non-renewable resource, and it is, rather, the distribution of potable and irrigation water which is scarce, rather than the actual amount of it that exists on the earth. Water-poor countries use importation of goods as the primary method of importing water (to leave enough for local human consumption), since the manufacturing process uses around 10 to 100 times products' masses in water. In the developing world, 90% of all wastewater still goes untreated into local rivers and streams (UNEP, 2002). Some 50 countries, with roughly a third of the world's population, also suffer from medium or high water stress, and 17 of these extract more water annually than is recharged through their natural water cycles (Ravindranath and Sathaye, 2002). The strain not only affects surface freshwater bodies like rivers and lakes, but it also degrades groundwater resources.

The human body contains from 55% to 78% water, depending on body size. To function properly, the body requires between one and seven liters of water per day to avoid dehydration; the precise amount depends on the level of activity, temperature, humidity, and other factors. The UN World Water Development Report (WWDR, 2003) from the World
Water Assessment Program indicates that, in the next 20 years, the quantity of water available to everyone is predicted to decrease by 30%. 40% of the world’s inhabitants currently have insufficient fresh water for minimal hygiene. More than 2.2 million people died in 2000 from waterborne diseases (related to the consumption of contaminated water) or drought. In 2004, the UK charity Water Aid reported that a child dies every 15 seconds from easily preventable water-related diseases; often this means lack of sewage disposal. Therefore, the situation becomes alarming and availability of fresh water is an issue of concern around the globe.

The growing global shortages of clean water and the adverse serious consequences on the environment caused by the alarming rate of increase of wastewater necessitate the treatment and reduction of such wastewaters. It has become mandatory through the stringent environmental regulations and norms that these wastewaters collected from municipalities and communities is to be treated adequately as to meet the prescribed and stringent water quality standards before discharging into the aquatic environment.

Currently, there are several wastewater treatment technologies in use. However, despite the progressive advancement in a line of wastewater treatment, the existing water treatment systems have their limitations in several aspects. The wastewater treatment processes included in general the screening/skimming, followed by the biological/chemical treatment and the advanced treatment methods composed with disinfections. Hence, the treatment process comprises of several exhaustive steps needing a variety of treatment chemicals. The most serious negative aspect is perhaps the implications of environmental concerns associated with these processes. It is to be noted that sometimes the chemicals/oxidants used, caused release/discharge of harmful/toxic chemicals ultimately posing additional burden to the environment. Some of the chemical oxidants commonly used in wastewater treatment today include chlorine, hypochlorite and ozone. These chemicals are extensively employed because of their availability, perhaps cost effectiveness and relative
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efficiency as oxidants. However, their use in such environmental remediation poses several health concerns because the chemicals and the by-products occurred seem to be toxic. For instance, the use and the handling of chlorine and ozone in wastewater treatment is reported to be composed with potential dangers as it is contained with highly corrosive and toxic gases. Moreover, the chlorination and ozonation processes were associated with the formation of harmful disinfection by-products (DBPs), such as trihalomethanes and bromate from the use of chlorine and ozone in wastewater treatment (Hagg and Hoigne, 1983; Jiang, 2007; Rook, 1974). Many of these by-products are potential mutagens or carcinogens, and may be more toxic and more difficult to remove than the parent contaminant. Similarly, the use of hypochlorite also causes concern; it is used as chlorine source for water treatment at smaller operations, since it is inexpensive; hypochlorite is synthesized by using chlorine gas it readily decomposes back into chlorine upon heating or chemical mishandling.

Another drawback with the existing systems of wastewater treatment is the occurrence of excessive sludge which often contains various types of toxic chemicals, removal of which is therefore, an additional concern. Furthermore, a number of organic sulphides and amines produced during wastewater treatment contribute on-site odors creating nuisance for human life calling for new methods for H₂S control in municipal sanitary sewer systems and within the treatment plants, and industrial waste treatment facilities. Another ongoing major problem in wastewater treatment is severe corrosion of facility structures from contact with hydrogen sulfide gas or its oxidation products after contact with air. Equally important are the health risks from exposure to H₂S gas even for shorter periods of time; such exposure is reported to be the leading cause of death among sanitary sewer workers.

Consequently, the increasing demand of clean water, pressing the need of an efficient and effective wastewater treatment processes have led to a great search for more viable, environmentally benign wastewater treatment chemicals that could be an alternative of existing chemicals. Among a number of such alternative chemicals presently under
investigations, ferrate(VI), a higher oxidation state of iron, is one of the highly promising alternative green chemicals that has been attracting much attention over the years because of its exceptional functionalities as compared to other chemicals currently employed in wastewater treatment.

1.1. ENDOCRINE DISRUPTING CHEMICALS (EDCs) - POLLUTANTS IN AQUEOUS WASTE

Endocrine disrupting compounds (EDCs) are chemicals with the potential to elicit negative effects on endocrine systems of humans and wildlife (Campbell et al., 2006). The US Environmental Protection Agency (USEPA) defines an EDC as: “An exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior.” (USEPA, 1997). They are broadly classified into several categories, such as hormones (natural and synthetic estrogen or steroids), pharmaceuticals and personal care products (PPCPs), industrial chemicals, pesticides, combustion byproducts, and surfactants (Campbell et al., 2006; Giesy et al., 2002). The USEPA tried to establish the Endocrine Disruptor Screening Program (EDSP) to develop official screening methods and toxicity testing strategies for approximately 87,000 compounds. The European Organization for Economic Co-operation and Development (OECD) has made an effort to develop a reliable method to confirm the significance of EDCs (Hecker et al., 2007). However, the proposed methods have not yet fully accepted within scientific communities (Snyder et al., 2003).

Despite of great efforts to prepare official/acceptable guidelines of EDCs, their definition and terms are still found ambiguous. Although many natural and synthetic chemicals have been widely considered as EDCs, numerous chemicals present in the environment still remain unidentified and are considered suspicious as potential EDCs (Chang
EDCs have been attributed to disturb the reproductive system in humans and wildlife (Colborn et al., 1993, Hayes et al., 2002, Oak et al., 2004, Samir et al., 2006 and Campbell et al., 2006). Human exposure to these chemicals in the environment is a critical concern with unknown long-term impacts. Natural and synthetic EDCs are released into the environment by humans, animals and industry; mainly through sewage treatment systems before reaching the receiving bodies (soil, surface water, sediment and ground water) (Liu et al., 2009). It is further reiterated that several EDCs are found potential to show estrogenic response even at very low concentrations (parts per billion to parts per trillion). Therefore, the low level presence of these chemicals in wastewater, surface waters, sediments, groundwater, and even drinking water is a great concern for environmentalist (Benfenati et al., 2003, Petrović et al., 2003, Snyder et al., 2003 and Petrović et al., 2004). Wastewater treatment plants have been studied as a major source for EDCs (Kolpin et al., 2002 and Snyder et al., 2003, Campbell et al., 2006).

1.1.1. BISPHENOL A (BPA)

![Structure of Bisphenol A (BPA)](image)

**Figure 1.1.** Structure of Bisphenol A (BPA).

Bisphenol A has become ubiquitous in the environment for the last past 80 years because of its presence in a multitude of products including food and beverage packaging, flame retardants, adhesives, building materials, electronic components, and paper coatings (Oehlmann et al., 2009; Staples et al., 1998). This releases through chemical manufacture, transport and processing. Post-consumer release is primarily via effluent discharge from municipal wastewater treatment plants, leaching from landfills, combustion of domestic waste, and the natural breakdown of plastics in the environment (Crain et al., 2007; USEPA, 2010). Release of BPA to the environment exceeds one million pounds per year (USEPA, 2010).
The tolerable daily intake for BPA was established at 25 μg/kg bodyweight/day by Health Canada and 50 μg/kg bodyweight/day by the United States and the European food safety authority (EFSA) (Rochester, 2013; Krishnan et al., 2010), but EFSA recommended the current tolerable daily intake (TDI) be lowered from its current level of 50 μg/kg bw/day (or 0.05 mg/kg/bw/day) to 5 μg/kg bw/day (0.005 mg/kg/bw/day) (EFSA, 2014).

BPA occurs at relatively high concentrations (up to 21μg/L) in the rivers and lakes worldwide (Crain et al., 2007). In China, BPA is up to 0.19 μg/L in the surface seawaters, 3.92 μg/L in rivers/lakes/ponds, and 370 μg/L in wastewaters (Huang et al., 2012; Zhang et al., 2014). In order to gain basic understanding of the effects of BPA, many research groups are currently testing its effects on wildlife. Several studies have reported that BPA at higher concentrations caused several adverse effects especially on reproduction. For example, in the freshwater ramshorn snail (Marisa cornuarietis), exposure levels >1.0 mg/L were found to result in superfeminization (additional female organs, enlarged sex glands, oviduct deformities, and increased fecundity), oviduct rupture and mortality (Oehlmann et al., 2000).

In the mollusc Mytilus edulis, spawning induction, as well as oocyte and ovarian follicle damage, was observed following BPA exposure for 3 weeks at 50 mg/L (Aarab et al., 2006). Alo et al., (2005) found that 80 mg/L BPA altered the activity of neural estrogen receptors that regulate growth of hormone in Mediterranean rainbow wrasse (Coris julis), potentially impairing reproduction and development in this sequentially hermaphroditic species. Fathead minnows exhibited altered sex cell type ratios (increased percentage of spermatocytes) following 1 mg/L BPA exposure, and reduced numbers of mature spermatozoa at 16 mg/L (Sohoni et al., 2001). Altered sex steroid levels were also found in the marine turbot (Psetta maxima) after exposure to BPA concentration of 59 mg/L (Labadie and Budzinski, 2006). Furuya et al. (2002) reported delayed growth of comb, wattle, and testes in male chickens that received oral doses of BPA as low as 2 mg/1000 g body weight every two days for up to 23 weeks. In field voles (Microtus agrestis) exposure to 250 mg/kg/day resulted in increased
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testosterone levels (Nieminin et al., 2002). Studies of the effects of BPA exposure on mammal currently relies on data from laboratory studies on model organisms, which indicate many adverse effects on rodents at high BPA levels. Such effects include advanced puberty (Howdeshell et al., 1999), increased obesity (Grün and Blumberg, 2009), pregnancy complications (Berger et al., 2008), defects in male and female reproductive organs (Richter et al., 2007), prostate effects and increase in malignancies (Hunt et al., 2009).

1.1.2. DICLOFENAC SODIUM SALT (DFS)

![Structure of diclofenac sodium salt (DFS).](image)

Diclofenac [2-(2,6-dichloranilo)phenyl acetic acid] is a phenyl acetic acid derivative that is a non-steroidal anti-inflammatory drug (NSAID) with analgesic, anti-inflammatory, and antipyretic properties. The sodium salt of diclofenac was used to treat osteoarthritis, rheumatoid arthritis, ankylosing spondylitis, and mild to moderate pain (Chae et al., 2015). It is also recommended to reduce menstrual pain, dysmenorrhea etc. (Vogna et al., 2004; Zhang et al., 2008). Since then, diclofenac is the most commonly used analgesic in the world and is commercially available in various formulations including ones for oral administration. The global consumption of diclofenac is estimated to be approximately 1000 tons per year (Zhang et al., 2008), with a defined daily dose of 100 mg (Fent et al., 2006). Approximately 65% of the dosage is excreted through urine, mainly as hydroxylated metabolites conjugated to glucuronides after enterohepatic circulation (Zhang et al., 2008 and Kenny et al., 2004). However, the actual amount of metabolites in the feces is still not clear. DFS is generally removed by only about 30% in conventional sewage treatment plants (STPs) (Suarez et al., 2008). Because of its low biodegradability (Joss et al., 2006) and its limited sorption
properties onto activated sludge (Ternes et al., 2004), DFS has been detected in STP-effluent and surface water up to 4.7 μg/L and 1.2 μg/L, respectively, and even in groundwater and tap water at concentrations up to 380 ng/L and below 10 ng/L, respectively (Aguinaco et al., 2012 and Heberer, 2002), which highlighted that the effects cited are of sufficient magnitude to suspect chronic toxicity in aquatic organisms. Diclofenac is significantly found in rivers, groundwater, hospital effluents and in drinking water (Santos et al., 2010). DFS is considered to be one of the most relevant compounds in terms of ecotoxicity and persistence in the environment.

Recent studies have shown that diclofenac inhibits the activity of cyclooxygenases and DNA synthesis through multiple mechanisms (Mastrangelo et al., 2000; Elron-Gross et al., 2008). Diclofenac has been proven as a pregnancy risk class C drug by the United States Food and Drug Administration (FDA). Even though the toxicity and teratogenicity of diclofenac were measured, conflicting data is published for different animal model systems. Fetal neuronal cells apoptosis is significantly induced in diclofenac-treated pregnant rats (Gokcimen et al., 2007). Additionally, diclofenac-treated rodents deliver fetuses with severe morphological abnormalities such as defects of the palate, limbs, and ductus arteriosus (Zenker et al., 1998; Chan et al., 2002). Diclofenac-treated medaka fish embryos also have decreased survival rates, shrunken yolks, and hemorrhage (Nassef et al., 2010). Furthermore, myofibril misalignment occurs in diclofenac-treated zebrafish embryos via disruption of actin organization (Chen et al., 2011) and alteration of mRNA expression (Felice et al., 2012). These studies clearly suggest diclofenac toxicity during embryogenesis, although it seems to be safe for embryos at considerably low doses.

Diclofenac is thought to affect damage in renal and gastrointestinal tissue in several vertebrate taxa (Haap et al., 2008) and its accidental exposure in the veterinary use has resulted in the near extinction of critically endangered Asian vulture populations. This causal relationship was subsequently confirmed under controlled experimental conditions in both
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captive Asian and African white-backed vultures (*G. africanus*) (Oak *et al*., 2004; Swan *et al*., 2006b). For this reason diclofenac was highlighted by the European Environment Agency (EEA, 2010) and several authors (Fent *et al*., 2006; Letzel *et al*., 2009) as being of particular environmental concern. Saravanan *et al*., (2011) recently reported that diclofenac interferes with the biochemical functions of fish and leads to tissue damage even at environmentally relevant concentrations.

Ng *et al*. (2008) were able to demonstrate that DFS could induce cellular apoptosis. In addition diclofenac showed to induce uricemia in the chicken (Berger *et al*., 1960; Naidoo *et al*., 2007). Zebra mussels exposed to the environmentally relevant (nominal) concentration of 1 μg/L of diclofenac showed signs of oxidative stress with elevated lipid peroxidation levels. At a higher concentration 1000 μg/L, the defence mechanism of Glutathione S-transferase (GST) and mechanical translation (MT) were induced by diclofenac (Quinn *et al*., 2011; Schmidt *et al*., 2011). Among the NSAID, diclofenac showed the most acute toxic nature with effects being observed at concentrations below 100 mg/L (Cleuvers, 2003). Chronic toxicity trials performed on rainbow trout (*Oncorhynchus mykiss*) evidenced cytological changes in the liver, kidneys and gills after 28 days of exposure to just 1 μg/L of diclofenac. For a concentration of 5 μg/L renal lesions were evident as well as drug bioaccumulation in the liver, kidney, gills and muscles (Schwaiger *et al*., 2004; Triebskorn *et al*., 2004). Brown trout (*Salmo trutta f. fario*) showed similar cytological damage and a reduction of haematocrit values after 21 days of exposure to 0.5 μg/L of this active substance (Hoeger *et al*., 2005). Schmitt-Jansen *et al*. (2007) evaluated both diclofenac phytotoxicity and its photochemical products on the unicellular chlorophyte *Scenedesmus vacuolatus*. Inhibition of algal reproduction by the parent compound only occurred at a concentration of 23 mg/L, hence indicating no specific toxicity. However, the threat significantly increased when metabolites were produced from 53 h of exposure to daylight. Diclofenac also inhibited the growth of...
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marine phytoplankton *Dunaliella tertiolecta* for concentrations of 25 mg/L and above. For this organism, 96 h EC\textsubscript{50} of 185.69 mg/L was found (DeLorenzo and Fleming, 2008).

1.1.3. 17α-ETHYNYLESTRADIOL (EE2)

![Structure of 17α-ethynylestradiol (EE2).](image)

17α-ethynylestradiol, also known as EE2 (19-nor-17α-pregna-1,3,5(10)-trien-20-yn-3, 17-diol) is a synthetic estrogen compound and is a derivative from the natural hormone, estradiol (E2). EE2 is used in almost all modern formulations of combined oral contraceptive pills and hormone replacement therapy for treatment of osteoporosis, menstrual disorders, and prostate and breast cancer and other cancer ailments (Datapharm, 2008; USFDA, 2012a; Han et al., 2013; Aris et al., 2014), to improve productivity by promoting growth, prevent and treat reproductive disorders in livestock (Gadd et al., 2010; Liu et al., 2012), to develop single-sex populations of fish to optimize the growth in aquaculture (Körner et al., 2008; Kuster et al., 2005). A survey on best-selling drugs published by Pharmacy Times\textsuperscript{®} in 2010 found that EE2 was used as an active pharmaceutical ingredient in five of the top 200 prescribed drugs in the U.S. under different brand names (Bartholow, 2011). Mazellier et al. (2008) stated that EE2 is used for the treatment of estrogenic deficiencies and oral contraceptives with doses ranging from 15 to 50 µg tablet. In France, EE2 is widely used by women (30–40µg per bill) and about 60% ranging from 20–44 years old (Muller et al., 2010).

Humans and livestock excrete a considerable quantity of hormones. Human urine is considered as one of the main source of EE2 (Pauwels et al., 2008; Vethaak et al., 2005). The combined farm animal population, for example, sheep and poultry, generates around four times more estrogens than the human population in the UK (Johnson et al., 2000) and the
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Annual level of estrogen excretion by farm animals reached approximately to 33 tons in the European Union and 49 tons in the United States (Tang et al., 2013). These hormones penetrate the surface and ground water systems through sewage treatment plants, septic systems, from the industrial sources that run the synthetic hormone production facilities, from aquaculture runoff, and through agricultural runoff when sewage and manure are used as fertilizer (Aris et al., 2014). In fact, treated sewage effluents constitute the major source of environmental EE2 due to the inadequate removal of EE2 in STPs (Braga et al., 2005; Johnson and Sumpter, 2001). Orally ingested EE2 undertakes extensive metabolism in liver, principally via oxidation at C17 ethinyl triple bond and aromatic hydroxylation at C2/C4 on steroid nucleus, prior to excretion via urine and feces. Human metabolism transforms EE2 into biologically inactive sulfate and glucuronide forms (Bolt, 1979; Han et al., 2013). However, partial degradation in sewage treatment plants (STPs) and natural environment deconjugates EE2 metabolites and renders them estrogenically active again (Limpiyakorn et al., 2011; Atkinson et al., 2012). Larcher and Yargeau (2013) explained that the treatment process in wastewater treatment plants is incomplete and insufficient to remove EE2 resulting in measured waste water treatment plant (WWTP) effluent concentrations is up to 62 ng/L. Cargouët et al. (2004) also reported that the highest level of free EE2 was detected in domestic wastewater at 7 ng/L and in the effluent of wastewater treatment plants of up to 42 ng/L. Li et al. (2013) estimated that the concentration of EE2 in reclaimed water would still be 8.7 ng/L, which was much higher than the predictive non-effect concentration (PNEC) of EE2 (0.002 ng/L) even though the effluent of WWTP in China with a treatment capacity of 200,000 m$^3$/d was treated by ozonation and microfiltration to produce reclaimed water. Hence, EE2 was detected in treated drinking water and was found be 0.5 ng/L in the German drinking water (Atkinson et al., 2012; Nasuhoglu et al., 2012).

Similarly, the Endocrine Disruptor Knowledge Base (EDKB) (USFDA, 2012b), which is jointly published by the U.S. Food and Drug Administration (FDA) and National Center for
Toxicological Research, identifies EE2 as the most potent estrogenic chemical in all endocrine-disrupting chemicals discovered to date. In January 2012, the European Commission announced a proposal to limit EE2 in European water bodies to an annual average below 0.035 ng/L under its Water Framework Directives, which has sparked wide debate due to the potentially high treatment costs (McKie, 2012; Owen and Jobling, 2012). In Australia, the risk of human exposure to EE2 through affected drinking water is a real concern in water-stressed regions where drinking water supply is augmented by recycled water produced from municipal wastewater effluents (Ying et al., 2004). The Australian Guidelines for Water Recycling recommends a maximum level of 1.5 ng/L EE2 in drinking water (Middleton et al., 2008; Han et al., 2013). Previous studies have reported the ability of EE2 to affect the endocrine system of exposed biota by altering sex determination, delaying sexual maturity and decreasing secondary sexual characteristics even at low concentrations (ng/L) (Chen et al., 2010; Dziewczynski and Hebert, 2013; Liu et al., 2012c). EE2 showed the highest estrogenic potency in the in vitro tests compared to the other estrogens E2 and E1 (Andrew et al., 2010; de Mes et al., 2005; Colman et al., 2009). However, the toxicity of EE2 varies and is dependent on the studied species, whether in vitro or in vivo assays are used (Robinson and Hellou, 2009).

The toxic potential of estrogen compounds to various organisms has been extensively studied. Numerous experiments proved that EE2 was very toxic to a large number of exposed organisms. The recent work enables comparative toxic effects of EE2 with several natural estrogen compounds viz., E1, E2 and E3 (Aris et al., 2014). Endocrine-disrupting effects of EE2, both in vivo (Thorpe et al., 2003) and in vitro (Harris et al., 2011; Thorpe et al., 2009), was obtained in freshwater fish species both in laboratory and field studies at the level of nanogram per liter. The EE2 route of exposure can affect organisms through direct or indirect exposure (Aydin and Talinli, 2013). Several studies have shown that exposure to concentrations of EE2 in the range of those detected in the environment (0.001–0.273 mg/L)
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(Ternes et al., 1999; Kolpin et al., 2002) elicits the synthesis of the egg-yolk precursor vitellogenin, increases incidences of histological aberrations, and causes the feminization of male fish (Harries et al., 1996; Palace et al., 2006; Dussault et al, 2009). This causes directly or indirectly to reduce the fate of survival, the growth of early-life stage of organisms, and reproductive success (e.g., fertility and hatching success), and also impact on the population level (Yan et al., 2012).

Other than aquatic organisms, vertebrates including mammals have also been shown to be sensitive to EE2, particularly during their postnatal development (PND). For example, Vosges et al. (2008) reported that male rats that were exposed to EE2 in their drinking water for 3 weeks at a concentration of 0.1 and 1 mg/L (PND 22–PND 43) were greatly affected with their ponderal growth. The males exposed to 10 ng/mL EE2 in drinking water from PND 5 onwards conceived a significant higher proportion (25%) of small litters (one to five pups) than the control males (0–3%). Delclos et al. (2009) reported that 50 ppb of EE2 can affect the exposed Sprague Dawley rats, by decreasing body weight, accelerating the vaginal opening, and altering the estrous cycles in young animals. At higher doses, anogenital distance was subtly affected and significantly increased the incidence of uterine lesions (atypical focal hyperplasia and squamous metaplasia). Exposure during development (from gestational day 7 to postnatal day 8) to oral micromolar doses of EE2 permanently disrupted the reproductive tract of male rats (Larcher et al., 2012).

1.1.4. 4-TERN-OCYLPHENOL

A great number of contaminants emitted to the natural environment are responsible for harmful effects on ecosystems. Some of the anthropogenic chemicals are affecting greatly the
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endocrine systems of vertebrates and invertebrates by mimicking their hormones (Lintermann et al., 2003, Campbell et al., 2006). In a line, one of the predominant EDC is alkylphenol ethoxylates (APEs) and their metabolites (nonylphenol and octylphenol). The IUPAC name of nonylphenol is 4-(2,4-dimethylheptan-3-yl) phenol and octylphenol is 4-(1,1,3,3-Tetramethylbutyl) phenol. They are widespread in the environment and have been detected worldwide in surface waters, effluents of sewage treatment plants, sediments, soil, air and organism tissues (Ying et al., 2002; Ospar, 2006; Quednow and Puttmann, 2008). APEs are non-ionic surfactants and widely used in a variety of industrial, household and commercial applications for over 60 years (Gadzała-Kopciuch et al., 2008). Moreover 4-tert-octylphenol is used in production of phenol/formaldehyde resins (Ospar, 2006). The worldwide average production of APEs was reached to 390,000 Mg/year (Lintermann et al., 2003). In the UK alone 16,000–19,000 Mg of APEs are consumed annually, of which 6,500 Mg (37%) are estimated to be released into the aquatic environment (Blackburn, 1995). In wastewater treatment plants as well as in the environment, APEs are fairly quickly biodegraded by removal of ethoxy groups, producing more persistent products: alkylphenols such as nonylphenol, octylphenol and alkylphenol mono-, di- and tri-ethoxylates. The low solubility of these products as well as the presence of benzene rings are responsible for their relatively low level of microbial degradation (Lintermann et al., 2003; Ying et al., 2002; Ning et al., 2007). Octylphenols concentrations measured in surface waters was found to be as high as 0.43 μg/L. In wastewaters from industrial and municipal sewage treatments plants, octylphenol content was in the range from 0.17 μg/L to 9 μg/L, and occasionally up to 195 μg/L (Ospar, 2006). The contaminant was also found in drinking water (0.06 μg/L) (Gibs et al., 2007). Research on biodegradation of octylphenol within the water phase revealed that its half-life varies between 7 to 50 days. In anaerobic sediments, however, octylphenol is not biodegradable (Johnson et al., 2000). The low solubility of octylphenol and octanol-water partition coefficient (logK_{OW}) value suggested assuming the contaminant tends to bind to
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organic matter in sediments. Measurements showed that sediments can contain up to several hundred times more octylphenol than the corresponding surface water (Ying et al., 2002).

Among the APEs group of compounds, 4-tert-octylphenol has the greatest estrogenic potency. Although 4-tert-octylphenol is about 1500 times less potent than 17β-estradiol (Ning et al., 2007a) however, possesses greater tendency to accumulate in sediments and bioaccumulation within the lipids of water organisms (Ferreira-Leach and Hill, 2001). Additionally, widespread industrial emission of this compound leads to consider it as a high risk pollutant.

1.1.5. POTASSIUM PHTHALATE

![Structure of potassium phthalate.](image)

Potassium hydrogen phthalate, often called KHP, is an acidic salt compound. It forms white powder, colorless crystals, a colorless solution, and an ionic solid that is the monopotassium salt of phthalic acid. The hydrogen is slightly acidic, and it is often used as a primary standard for acid-base titrations because it is solid and air-stable, making it easy to weigh accurately. It is not hygroscopic. It is also used as a primary standard for calibrating pH meters because, besides the properties just mentioned, its pH in solution is very stable.

Phthalate represents a large family of chemicals which are widely used as plasticizers, primarily in the production of polyvinyl chloride resins (Bemis et al., 1978). Dimethyl phthalate (DMP) is a short-chained ester with two carboxyl groups on the aromatic ring. It is typically used in cellulose-ester-based plastics, such as cellulose acetate and butyrate (Staples et al., 1997), and it is a component of paints, adhesives, printing inks and coatings. Due to its wide applications in industry and large quantities of use, DMP is recognized as a significant
environmental contaminant and is commonly detected in natural ecosystems. Health and environmental concerns about this phthalate ester is recognized for many years, particularly in regard to its physiological and biochemical effects on organisms (Zhao et al., 2004; Wang et al., 2004). It is known as an endocrine-disrupting chemical which may promote chromosome injuries in human leucocytes and interfere with the reproductive system and normal development of animals and humans (Jobling et al., 1995; Allsopp et al., 1997). DMP is relatively a stable compound in the natural environment. The hydrolysis half-life is estimated to be about 20 yr (Staples et al., 1997). Studies of its biodegradation in fresh water, marine water, sediment, wastewater and sludge, have revealed a low degradation rate in the range of several days to a few months (Staples et al., 1997). Only a few results concerning DMP photolysis are available since phthalic acid dialkyl esters have been reported to be relatively photoresistant; for example, quantum yields of decomposition of phthalate <0.03 (Hizal et al., 1993). In view of this, it is necessary to identify a satisfactory treatment process for the effective destruction of this compound from contaminated waters and wastewaters.

1.2. OVERVIEW OF CONVENTIONAL WASTEWATER TREATMENT

The collection of storm water and drainage dates from ancient times, the collection of wastewater was traced only to the early 1800s and the development of the germ theory in the latter half of the nineteenth century as introduced by the Koch and Pasteur marked the beginning of new era in sanitation. Today, a typical wastewater treatment system comprises of unit operations or physical treatments. The unit processes referring to chemical treatments or biological treatments. The unit operations are grouped together to provide what is known as preliminary, primary, secondary and tertiary treatment. Preliminary treatment process is attempted to render the effluent suitable for further treatment and it consists of physical unit operations like screening and combination for the removal of debris and rags, grit removal for the elimination of coarse suspended matter and flotation for the removal of oil and grease.
Primary treatment involves the partial removal of suspended solids and organic matter from the wastewater by means of physical operations such as screening and sedimentation. Secondary treatment processes are used to convert the finely divided and dissolved organic matter in wastewater into flocculent settleable organic and inorganic solids. The purpose of secondary treatment is the removal of soluble and colloidal pollutants and suspended solids that have escaped the primary treatment and reduce BOD and COD through biological process. In these processes, micro-organisms, particularly bacteria, convert the colloidal and dissolved carbonaceous organic matter into various gases and into cell tissue leading to reduction of BOD and COD. This is typically done through processes, namely treatment by trickling filtration, activated sludge processes, oxidation ditch and oxidation ponds are some of the common secondary treatment procedures. Tertiary treatment goes beyond the level of conventional secondary treatment for purification of wastewater i.e. removal of significant amounts of nitrogen, phosphorus, heavy metals, biodegradable organics, bacteria and viruses. In addition to biological nutrient removal processes, other unit operations like chemical coagulation, flocculation and sedimentation, followed by filtration and activated carbon are frequently used. Less frequently ion exchange and reverse osmosis for specific ion removal or for dissolved solid reduction are used (Prabul et al., 2011).

Although the conventional water and wastewater treatment processes are long been established in removing many chemical and microbial contaminants of concern to public health and the environment, the effectiveness of these processes are become limited over the last couple of decades because of three new challenges (Langlais et al., 1991; Mallevalle et al., 1996). First, increased knowledge about the consequences from water pollution and the public desire for better quality water have promoted the implementation of much stricter regulations by expanding the scope of regulated contaminants and lowering their maximum contaminant levels (MCLs). In water treatment, among the most important developments are the establishment of the possible link between halogenated disinfection by-products (DBPs)
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and cancers, and the recent outbreaks caused by *Giardia* cysts and *Cryptosporidium* oocytes. The second factor is the diminishing water resources and rapid population growth and industrial development. The reuse of municipal and industrial wastewaters and the recovery of potential pollutants used in industrial processes become more critical. In addition, advances in the manufacturing industry and the growing market associated with advanced treatment processes have resulted in substantial improvements to the versatility and costs of these processes at the industrial scale. In addition, advances in the manufacturing industry and the growing market associated with advanced treatment processes are resulted in substantial improvements to the versatility and costs of these processes at the industrial scale.

To resolve these new challenges and better use economical resources, various advanced treatment technologies is being proposed, tested, and applied in recent times to meet both current and anticipated treatment requirements. Among these, membrane filtration, advanced oxidation processes (AOPs), and UV irradiation have shown successfully to remove a wide range of potential water contaminants and hold great promise in water and wastewater treatment technologies.

1.3. **OXIDATION PROCESSES IN WASTEWATER TREATMENT**

1.3.1. **Chemical oxidation systems with direct attack of oxidant**

**Ozonation**

In wastewater treatment, ozone acts as a powerful disinfectant and a strong oxidant. Being a very powerful oxidizing agent (E° = 2.07 V), it can react with most species containing multiple bonds (such as C=C, C=N, N=N, etc.), but not with singly bonded functionality such as C–C, C–O, O–H at high rates. This is mainly due to the fact that there is no easy chemical pathway for the oxidation to take place. However, ozone does react with simple oxidizable ions such as S²⁻, to form oxyanions such as SO₃²⁻ and SO₄²⁻. Ozone show low solubility and it is usually generated on-site from dry air or pure oxygen through high-voltage corona
discharge. Once dissolved into water, it undergoes very complex self-decomposition and oxidation reactions. As a disinfectant, ozone has been long recognized to inactivate coliform indicators effectively and other bacteria from municipal waters. More resistant pathogenic microorganisms such as Giardia sp. and Cryptosporidium sp. are inactivated in waste waters by employing the ozone dose. The effectiveness of ozone was compared with other common disinfectants was well discussed and documented elsewhere (Sobsey, 1989). Moreover, the reaction mechanisms were not yet firmly established. It was generally accepted that the inactivation was achieved mostly by the attack of molecular ozone instead of free radicals (NRC, 1980).

One major concern associated with ozone application is that bromide ions in water can be oxidized into bromate ions and other harmful bromated organic by-products (Ozekin et al., 1997; Singer, 1990; Siddiqui et al., 1995; Song et al., 1997; von Gunten et al., 1996; Westerhoff et al., 1998). Bromate ions are classified as potential carcinogen by the International Agency for the Research on Cancer (IARC). Another concern is the potential increase in biological regrowth in water distribution systems by transforming high-molecular-weight organic compounds into low-molecular-weight organic compounds such as aldehydes, ketones, and carboxylic acids. Moreover, the additional limitation of the ozonation process is the relatively high cost of ozone generation process coupled with very short half-life period of ozone. Thus, ozone needs to be generated always on site. Further, the process efficiency is severely dependent on the efficient gas liquid mass transfer, which is quite difficult to achieve due to the low solubility of ozone in the aqueous solutions.

1.3.2. Advanced Oxidation Processes (AOP)

Advanced oxidation processes (AOPs) have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical (·OH), as the primary oxidant (Glaze, 1987). The ·OH radical is among the strongest
oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rates of contaminant oxidation. The generation of \( \cdot \)OH radicals is commonly accelerated by combining ozone (O\(_3\)), hydrogen peroxide (H\(_2\)O\(_2\)), titanium dioxide (TiO\(_2\)), heterogeneous photocatalysis, UV radiation, ultrasound, and (or) high electron beam irradiation. Of these, O\(_3\)–H\(_2\)O\(_2\), O\(_3\)–UV, H\(_2\)O\(_2\)–UV, and heterogeneous photocatalytic processes hold the greatest promise to detoxify water and wastewater. Ozone at elevated pH will be decomposed into hydroxyl radicals.

**Ozone – hydrogen peroxide (Peroxone)**

Although H\(_2\)O\(_2\) reacts very slowly with the ozone molecule in water, its conjugate base (HO\(_2\)) can rapidly react with molecular ozone, thereby initiating the formation of hydroxyl radicals in two steps (Glaze, 1987). The O\(_3\)–H\(_2\)O\(_2\) process, often called the PEROXONE process, is used most widely in practice among the AOPs except for ozonation because of simplicity and low radical generation costs. In water treatment, the O\(_3\)–H\(_2\)O\(_2\) process is mainly used for the oxidation of micro-pollutants, the removal of pesticides, and the control of taste- and odour-causing materials (Ferguson *et al.*, 1990; Karimi *et al.*, 1997). The optimum H\(_2\)O\(_2\) to O\(_3\) ratio usually ranges from 0.3 to 0.6. It was also tested for contaminated groundwater and wastewater treatment. Murphy *et al.* (1993) studied the removal of colour from three effluent streams from a pulp and paper mill. They reported that the O\(_3\)–H\(_2\)O\(_2\) process could achieve colour removal up to 85% for the caustic extract stream, up to 90% for the acidic stream, and up to 50% in the final effluent.

**Ozone – Ultraviolet radiation**

The O\(_3\)–UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals (Peyton and Glaze, 1982a & 1982b, 1988). Because the maximum absorption of ozone molecule is at 253.7 nm, the light source
commonly used is a medium-pressure mercury lamp wrapped in a quartz sleeve. It can
generate the UV light at a wavelength of 200–280 nm. The O$_3$–UV process was initially
developed by Prengle et al. (1980) and patented by Garrison et al. (1975) for the destruction
of wastewaters containing cyanides. Since then, it was used to oxidize aliphatic and aromatic
chlorinated organic contaminants (Glaze, 1987), NOM (Peyton and Glaze, 1982b), and
pesticides (Beltrán et al., 1994a, 1994b). The results often showed that the O$_3$–UV process
was more effective than ozone alone in terms of reaction rate and removal efficiency. Its use
for the treatment of clear groundwater containing trichloroethylene (TCE) and
perchloroethylene (PCE) was already commercialized by early 1980s. However, the O$_3$–UV
process is now considered less economical compared to the O$_3$–H$_2$O$_2$ and H$_2$O$_2$–UV processes
in most cases.

**Hydrogen peroxide – Ultraviolet**

Under UV irradiation, H$_2$O$_2$ will be photocatalyzed to form two hydroxyl radicals. The
formed hydroxyl radicals then react with organic contaminants or undergo an H$_2$O$_2$
decomposition–formation cycle (Crittenden et al., 1999). Unlike ozone, H$_2$O$_2$ has an
exceptionally low molar absorptivity within the wavelength range of 200–300 nm. Thus, it is
particularly susceptible to the competing absorption of UV by organic compounds and
suspended solids in water. If organic compounds after activation could more rapidly react
with H$_2$O$_2$, such direct photo-oxidation would be expected to have a major contribution to the
overall degradation in the H$_2$O$_2$–UV system. Like the O$_3$–UV process, the H$_2$O$_2$–UV process
is mainly used for the oxidation of refractory contaminants. For example, Beltrán et al. (1993)
studied the H$_2$O$_2$–UV oxidation of atrazine in water. Results showed that, depending on the
initial atrazine concentration, more than 99% of the atrazine was degraded in less than 15 min.
Heterogeneous photocatalytic processes

Heterogeneous photocatalytic processes use certain metal oxides that can readily generate hydroxyl radicals on the surface of particles when absorbing UV light. The anatase form of TiO$_2$ possesses low band-gap energy (approximately 3.2 eV), which is almost equivalent to 400 nm wavelength of light. Hence, the most important heterogeneous photocatalytic processes include TiO$_2$–UV and TiO$_2$–H$_2$O$_2$–UV. Heterogeneous photocatalytic processes are an emerging technology. Their applications in oxidizing refractory organic contaminants still remain mostly at the laboratory scale. Wang and Hong (1999) demonstrated that the TiO$_2$-based process is very effective in removing polychlorinated biphenyls (PCBs).

Fenton oxidation

The oxidation system based on the Fenton’s reagent (hydrogen peroxide in presence of a ferrous salt) is used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning etc. (Bigda, 1996). The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater streams but the nature of these species is still under discussion and its formulation is a subject of controversy in the past and recent Fenton oxidation related literature (Bossmann et al., 1998; Walling, 1998; MacFaul et al., 1998; Pignatello et al., 1999). In the literature, three main reactive radical species have been contemplated; Two of them involve the presence of hydroxyl radicals (classical Fenton’s chemistry) in either ‘free’ or ‘caged’ form (Walling and Amarnath, 1982) whereas third oxidant is postulated to be aquo or organocomplexes of the high valence iron, the ferryl ion (Sauer and Ollis, 1996). The rate of this reaction should be strongly dependent on the presence of radical scavengers such as $t$-butanol but in some cases substantial decrease is observed even at high concentrations of
these species (Rahhal and Richter, 1988). This led to some investigations relating to the presence of additional oxidant species using analysis of product distribution, EPR-spin trapping techniques, effect of added substrates. It should be noted at this stage that both hydroxyl as well as ferryl complexes coexist in Fenton’s mechanism and depending on the operating conditions (substrate nature, metal–peroxide ratio, scavenger addition etc.). Nevertheless, the system is most suitably applicable to discoloration and or removal of odor ingredients with good energy efficiency. Also, the oxidation system is effectively used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for a secondary biological treatment (Chen and Pignatello, 1997).

1.4. FERRATE(VI)

Iron commonly exists as metallic iron (Fe), ferrous (Fe\(^{2+}\)), and ferric (Fe\(^{3+}\)) forms in the natural environment. However, the higher oxidation states of iron, i.e., \(+4, +5, +6\) and \(+8\) are known in certain environments. These higher oxidation states of iron are collectively known as ferrates. Among these ferrates, the \(+6\) state is relatively stable, easy to synthesize and is known to be obtained in the form of stable salts (Thompson et al., 1951; Audette and Quail, 1972; Bielski, 1991). Hence, during the last couple of decade greater interest and several research studies was conducted using the \(+6\) state of iron. Ferrate(VI) was first prepared in 1715 by Stahl when he conducted an experiment detonating a mixture of saltpeter and iron filings, and dissolved the molten residue in water. This colored solution was subsequently identified as potassium ferrate(VI), K\(_2\)FeO\(_4\). Eckenber and Becquerel in 1834 detected the same color when they heated red mixtures of potash (potassium hydroxide) and iron ores. Similarly, in 1840, Fremy hypothesized this colour to be an iron species with high valence, but its formula was suggested FeO\(_3\) (Jiang and Lloyd, 2002). With the development of more efficient synthesis and analytic methods of ferrate(VI) by Schreyer and coworkers (Thompson et al., 1951; Okerman and Schreyer, 1951). In the late 1950s, the chemistry of
ferrate(VI) and its application was much more explored. There are three common synthetic methods employed in the preparation of ferrate(VI): wet oxidation, dry oxidation and electrochemical methods. Of the several ferrate(VI) salts prepared, K$_2$FeO$_4$ is mostly used for various purposes due to its relatively easy synthetic route and stability towards spontaneous decomposition to ferric oxide (Sharma et al., 2002). Due to its high oxidizing capacity, ferrate(VI) has gained much attention in four different areas of research viz., environmental remediation as multipurpose chemical (i.e., oxidant, coagulant, disinfectant, antifouling oxidant etc.), cathode material for batteries (i.e., super iron battery); Green synthesis oxidant (i.e., selective organic synthesis); and source of hypervalent iron (i.e., several biochemical research as to use more powerful oxidant) etc.

i. Structure

According to X-ray powder pattern studies, ferrate(VI) showed tetrahedral structure in solid crystals such as K$_2$FeO$_4$, in which four equivalent oxygen atoms were covalently bonded to central iron atom in +6 oxidation state (Hoppe et al., 1982). The tetrahedral structure of ferrate(VI) was also confirmed in an aqueous solution by isotopic oxygen exchange study which showed that four oxygen atoms of ferrate(VI) were kinetically equivalent (Goff et al., 1971). Ferrate(VI) ions could possess three resonance hybrid structures in aqueous solution as shown in the following figure 1.6 (Norcross et al., 1997). Of the three resonance structures, the structures ‘1’ and ‘2’ were suggested as main contributors of ferrate(VI) based on theoretical studies of metal oxide structures.

**Figure 1.6.** Three resonance hybrid structures of ferrate(VI) ion in an aqueous solution (Norcross et al., 1997)
ii. Species in Aqueous Solution

Spectroscopic and kinetic studies have suggested that there exist four ferrate(VI) species in aqueous solution via their acid-base equilibrium (Rush et al., 1996). The species distribution of ferrate(VI) as a function of pH is indicated in the following figure 1.7, which indicates that HFeO$_4^-$ and FeO$_4^{2-}$ are predominant species in neutral and alkaline pH solution in which ferrate(VI) is known to be relatively stable towards its spontaneous decomposition to ferric ion (Fe(III)) (Tiwari et al., 2007; Lee and Gai, 1993).

![Figure 1.7. Species distribution of ferrate(VI) in aqueous solution (Tiwari et al., 2007)](image)

iii. Characterization and Quantification of ferrate(VI): UV/Vis Spectroscopy

The aqueous solution of ferrate(VI), which is red-violet in color and gives characteristic absorption maxima at around 500 and 800 nm can be used for its qualitative as well as quantitative estimation. Moreover, the aqueous solution of ferrate(VI) prepared in phosphate buffer between pH 9.0 and 10.5 are stable for hours makes it easy to obtain the spectral measurements at this pH. Figure 1.8 shows the UV-Vis absorbance spectrum in phosphate buffer solution (pH 9.2) as a function of ferrate(VI) concentrations. The spectrum showed its maximum absorption at wavelength of 510 nm. The molar extinction coefficient for FeO$_4^{2-}$ at pH 9.0 is reported to be 1150 M$^{-1}$cm$^{-1}$ (Sharma et al., 2001; Lee et al., 2004; Bielski and Thomas, 1987). The characteristic absorption of ferrate(VI) at the wavelength of 510 nm was conveniently used to measure the concentration of ferrate(VI) in aqueous solutions (Sharma, 2002).
iv. Stability and decomposition of ferrate(VI)

The stability of ferrate(VI) in aqueous solutions depends on several factors viz., ferrate(VI) concentration, temperature of the solution, co-existing ions, pH etc. (Johnson and Sharma, 1999). The dilute solutions of ferrate(VI) seems to be more stable than concentrated (Schreyer and Okerman, 1951). The solution of 0.025 M ferrate(VI) will remain 89% even after the 60 min but if the initial concentration of ferrate(VI) was increased to 0.03 M, almost all the ferrate ions will get decomposed within the same period of time i.e., 60 min. Other reports also demonstrated that a 0.01 M potassium ferrate solution decomposed to 79.5% over a period of 2.5 h, while a 0.0019 M potassium ferrate solution decreased to only 37.4% after 3 h and 50 min at 25 °C (Wagner et al., 1952). The stability of K$_2$FeO$_4$ in 10 M KOH is increased from hours to week if no Ni$^{2+}$ and Co$^{2+}$ impurities are present (< 1μM) (Stuart and Ghosh, 1999). However, nitrate salts of Cu$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Pb$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$, Mg$^{2+}$ and other salts including K$_2$Zn(OH)$_4$, KIO$_4$, K$_2$B$_4$O$_7$, K$_3$PO$_4$, Na$_2$P$_2$O$_7$, Na$_2$SiF$_6$, Na$_2$SiO$_3$, Na$_2$MoO$_4$ and Na$_2$WO$_4$ have no effect on the stability of K$_2$FeO$_4$ (Stuart and Ghosh, 1999). A 0.5 M K$_2$FeO$_4$ solution, containing KCl, KNO$_3$, NaCl and FeOOH was studied to observe the ferrate(VI) stability in presence of these salts. It was found that the ferrate(VI) decomposed rapidly in the initial stage and appeared relatively stable at low ferrate concentrations when KCl and KNO$_3$
were present (Schreyer and Okerman, 1951). Phosphate was shown to retard the ferrate(VI) decomposition. The spontaneous decomposition of ferrate(VI) in aqueous solutions was reported to be increased significantly with decreasing the solution pH. Figure 1.9 obtained using the 1 mM solution of K₂FeO₄ in aqueous solution showed that at pH ~5.0, just after 7 min, the ferrate(VI) was decomposed completely, however, at pH ~9.0 and ~10.0, it was fairly stable even after elapsed time of 20 min (Tiwari et al., 2007). Other studies, conducted with 2h test period, the concentration of potassium ferrate slightly decreased when it was in 6 M KOH, but decreased rapidly when it was in 3 M KOH. The ferrate solution prepared with buffer solution at pH 8 was more stable than that prepared at pH 7.0 (Schreyer and Okerman, 1951); 49% of the original potassium ferrate remained after 8 h when the pH was 7.0, and 71.4% of that remained after 10 h when the pH was 8.0.

![Figure 1.9](image)

**Figure 1.9.** The change of the ferrate(VI) concentration as a function of time at various pH values [Initial concentration of ferrate(VI): 1 mM] (Tiwari et al., 2007)

The ferrate salts when dissolved in water, oxygen is evolved and ferric hydroxide is precipitated as shown in the following equation 1.1 (Bielski, 1992).

\[
4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 8KOH + 3O_2 \quad \ldots (1.1)
\]

The rate of decomposition of ferrate(VI) was strongly pH dependent. The lowest rate of decomposition was occurred at pH higher than ~9.0-10.0, while it increased significantly at
lower pH values (Carr et al., 1985). The reaction kinetics followed second-order below pH 9.0, while first order above pH 10.0 (Lee and Gai, 1993). The decomposition of ferrate(VI) hence, described by the following equilibrium and kinetic models (Rush et al., 1996).

\[
2\text{H}_2\text{FeO}_4^+ \leftrightarrow [\text{H}_4\text{Fe}_2\text{O}_7]^{2+} + \text{H}_2\text{O} \quad k_2 = 3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \quad \ldots (1.2)
\]

\[
[\text{H}_4\text{Fe}_2\text{O}_7]^{2+} + 2\text{H}^+ + 6\text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_6^{4+} + 3/2 \text{O}_2 \quad \text{Fast step} \quad \ldots (1.3)
\]

\[
\text{H}_3\text{FeO}_4^{4+} + \text{H}_2\text{FeO}_4 \leftrightarrow \text{[diferrate]} \quad k_4 \approx 3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \quad \ldots (1.4)
\]

\[
2\text{H}_2\text{FeO}_4 \leftrightarrow \text{[diferrate]} \quad k_5 = 1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \quad \ldots (1.5)
\]

\[
\text{H}_2\text{FeO}_4 + \text{HFeO}_4^- \leftrightarrow \text{[diferrate]} \quad k_6 \approx 1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \quad \ldots (1.6)
\]

\[
2\text{HFeO}_4^- \leftrightarrow [\text{Fe}_2\text{O}_7]^{2-} + \text{H}_2\text{O} \quad k_7 = 2.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \quad \ldots (1.7)
\]

Reactions clearly showed that the forward reactions (1.2) to (1.7) except reaction (1.3) are relatively slow steps hence, could be the rate determining steps. The rate constants were then calculated for the self decomposition of ferrate(VI), which is to be second order reactions. The second order rate constants for the decomposition of ferrate(VI) to iron(III) in 5 mM phosphate/acetate buffers are obtained and shown in figure 1.10 (Rush et al., 1996).

![Figure 1.10](image_url)

**Figure 1.10.** The second-order rate constants for the decay of ferrate(VI) to iron(III) in 5 mM (phosphate/acetate) buffers (Rush et al., 1996)

### 1.4.1. Ferrate(VI): A multi purpose green chemical in wastewater treatment

Ferrate(VI) is an emerging multi-purpose wastewater treatment chemical and owing to its multifunctional properties, viz., oxidation, disinfection, coagulation and generation of
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environmentally safe by-products (Murmann and Robinson, 1974). The oxidative properties of ferrate(VI) forms the basis for its potential applications, in particular, the water remediation. Ferrate(VI) is a powerful oxidizing agent in an aqueous media. The redox potential of ferrate(VI) ions (E^0 \text{(FeO}_4^{2-} / \text{Fe}^{3+}) and E^0 \text{(FeO}_4^{2-} / \text{Fe(OH)}_3 are 2.20 and 0.72 at pH 1.0 and 14.0, respectively. Under the acidic conditions, the redox potential of ferrate(VI) is thus greater than ozone and is the strongest of all the oxidants/disinfectants, viz., ozone, hydrogen peroxide, hypochlorite, chlorine, perchlorate etc. practically used for water and wastewater treatments (Table 1.1). In aqueous medium ferrate(VI) decomposes to Fe(III) and oxygen is evolved which makes it highly reactive, at the same, produces ferric (Fe^{3+}) ion as a by-product (Equation 1.1). This reaction is of particular interest to water treatment because it provides a suitable mechanism for self-removal of ferrate from solution. In all oxidation reactions, the final iron product is the non-toxic ferric ion which forms hydroxide oligomers. Eventually flocculation and settling occurs which removes suspended particulate matter.

Several studies of water contaminant oxidation with ferrate(VI) demonstrated that ferrate(VI) is a strong oxidant capable of removing a number of organic pollutants, such as alcohol (Bartzatt \textit{et al.}, 1985; Rao \textit{et al.}, 1988; Delaude and Laslo, 1996; Norcross \textit{et al.}, 1997), carboxylic compounds (Bielski \textit{et al.}, 1994), amino-acids (Sharma and Bielski, 1991; Rush and Bielski, 1993), phenol (Rush \textit{et al.}, 1995), 1,2-Diols (Rao \textit{et al.}, 1991), organic nitrogen compounds (Carr \textit{et al.}, 1981; Carr and Erickson, 1988; Johnson and Hornstein, 1996; Johnson and Hornstein, 1998), aliphatic sulphur (Bartzatt and Carr, 1986), nitrosamines compounds (Bartzatt and Nagel, 1991), recalcitrant organics (Gulyas, 1997), thiourea (Sharma and Rivera, 1996; Sharma \textit{et al.}, 1999a & 1999b), thiosulphate (Johnson and Read, 1996), chlorine oxyanions (Carr and Mclaughlin, 1988) and hydrazine compounds (Johnson and Hornstein, 1994). Importantly, ferrate(VI) showed ability to oxidize 71 emerging contaminants like estrogens, bisphenol A, and pharmaceuticals present in water (Anquandah and Sharma, 2009; Lee \textit{et al.}, 2008; Lee \textit{et al.}, 2009; Lee \textit{et al.}, 2005; Lee and
Gunten, 2010; Li and Gao, 2009; Sharma et al., 2006a & 2006b; Sharma et al., 2008a; Sharma, 2008; Sharma et al., 2009a & 2009b). In addition to organic impurities, ferrate(VI) also effective in the degradation/removal of several inorganic contaminants, viz., cyanide, ammonia, hydrogen sulphide etc. (Sharma et al., 1998a & 1998b). Ferrate(VI) also acts as an effective disinfectant in wastewater treatment. Ferrate(VI) can achieve disinfection at relatively 75 low dosages over wide ranges of pH (Cho et al., 2006; Jiang et al., 2007; Sharma, 2007). Ferrate(VI) could enable to kill more than 99.9% of total coliforms (Sharma et al., 2005a). The results showed that ferrate(VI) could deactivated the Escherichia coli (E.coli) at lower dosages or shorter contact time than hypochlorite (Jiang et al., 2007).

Ferrate(VI) is also an efficient coagulant (in the form of Fe(III) produced from ferrate(VI) reduction). Treatment of water by ferrate(VI) reduces efficiently the turbidity of water, decreases the concentration of various metals in free form as well as complexed species, nutrients, radionuclides, and humic acids (Tiwari et al., 2008; Jiang and Lloyd, 2002; Jiang et al., 2009; Jiang and Sharma, 2008a & 2008b; Jiang et al., 2001; Jiang and Wang, 2003; Jiang et al., 2006; Joshi et al., 2008; Lee et al., 2009; Lee et al., 2003; Liu and Liang, 2008; Potts and Churchwell, 1994; Sharma et al., 2005a & 2005b; Stupin and Ozernoi, 1995). As an antifouling agent, ferrate(VI) further replaces several chemicals utilized for odor control of sludge, mainly aggressive odors caused by ammonia and sulphides (De Luca et al., 1996). Application of ferrate(VI) is found environmentally safe, showed effective in controlling the bio-film growth in condenser systems (Fagan and Waite, 1983) suggesting its usefulness as a biocide in controlling biofouling.

As such, ferrate(VI) is proved to possess multifunctional properties in the wastewater treatment. Besides being strong oxidant, effective disinfectant, coagulant and antifouling agent, ferrate(VI) is further termed as a ‘Green Chemical’ as the end product of ferrate(VI) treatment is non-toxic, environmentally benign species, i.e., Fe(III) as seen in equation 1.1. This green nature of ferrate(VI) is particularly interesting in environmental remediation.
making it a highly promising alternative candidate for replacing environmentally hazardous chemicals/oxidants often to be used in water and wastewater treatment technologies. Moreover, the existing wastewater treatment processes require additional coagulant/adsorbent doses to remove the non-degradable impurities e.g., metallic species etc. A single dose of ferrate(VI), however, can degrade degradable impurities without leaving harmful by-products, at the same time removing non-degradable impurities through coagulation by ferric ions generated. In this line, like ozone, ferrate(VI) does not react with bromide ion; so carcinogenic bromate ion is not produced in the treatment of bromide containing water (Zhou et al., 2009). Further, ferrate(VI) can complete oxidation reactions in shorter time periods than oxidations carried out by permanganate and chromate (Delaude and Laszlo, 1996; Khalilzadeh et al., 2007).

The novel multifunctional properties of ferrate(VI), therefore, demonstrated ferrate(VI) as a promising tool for an enhanced wastewater treatment to eliminate various organic or even inorganic impurities by ferrate(VI)-oxidation as well as to remove non-degradable impurities by iron(III) precipitation in a single treatment step. The use of ferrate(VI) may, therefore, provide a safe, convenient, versatile and cost effective alternative to current approaches for water, wastewater, and sludge treatment. Ferrate(VI) treatment is free from the toxic byproducts, ferrate is an environmentally friendly oxidant that represents a viable substitute for other oxidants. Therefore, ferrate has the distinction of being an "environmentally safe" oxidant and may be termed as ‘Green-Chemical’ and the Ferrate treatment as ‘Green treatment’.
Table 1.1. Redox potential for the different oxidants used in water and wastewater treatment

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Reaction</th>
<th>$E^0$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>$\text{Cl}_2(\text{g}) + 2e^- \leftrightarrow 2\text{Cl}^-$</td>
<td>1.358</td>
</tr>
<tr>
<td></td>
<td>$\text{ClO}^- + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{Cl}^- + 2\text{OH}^-$</td>
<td>0.841</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>$\text{HClO} + \text{H}^+ + 2e^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.482</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>$\text{ClO}_2(\text{aq}) + e^- \leftrightarrow \text{ClO}_2^-$</td>
<td>0.954</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>$\text{ClO}_4^- + 8\text{H}^+ + 8e^- \leftrightarrow \text{Cl}^- + 4\text{H}_2\text{O}$</td>
<td>1.389</td>
</tr>
<tr>
<td>Ozone</td>
<td>$\text{O}_3 + 2\text{H}^+ + 2e^- \leftrightarrow \text{O}_2 + 2\text{H}_2\text{O}$</td>
<td>2.076</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>1.776</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>1.229</td>
</tr>
<tr>
<td>Permanganate</td>
<td>$\text{MnO}_4^- + 4\text{H}^+ + 3e^- \leftrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$</td>
<td>1.679</td>
</tr>
<tr>
<td></td>
<td>$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$</td>
<td>1.507</td>
</tr>
<tr>
<td>Chromate</td>
<td>$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \leftrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$</td>
<td>1.33</td>
</tr>
<tr>
<td>Ferrate(VI)</td>
<td>$\text{FeO}_4^{2-} + 8\text{H}^+ + 3e^- \leftrightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>$\text{FeO}_4^{2-} + 8\text{H}_2\text{O} + 3e^- \leftrightarrow \text{Fe(OH)}_3 + 8\text{H}_2\text{O}$</td>
<td>0.70</td>
</tr>
</tbody>
</table>

1.5. REVIEW OF LITERATURE

The role of ferrate(VI) in the wastewater treatment was well demonstrated elsewhere (Sharma et al., 2005; Tiwari et al., 2005). In addition to degrade the organic or even inorganic pollutants from waste water it showed excellent property to kill a wide variety of bacteria and virus in water and wastewater treatment process. The use of ferrate(VI) was discussed as to disinfect the wastewater and it was found that the ferrate(VI) can reduce 50% more color (Vis$_{400}$-abs), 30% more COD, and kill 10% more bacteria in wastewater, compared to aluminium sulphate or ferric sulphate (Jiang and Panagoulopoulos, 2004).

A range of organic contaminants were oxidized readily by ferrate(VI). Alcohol (Noricross et al., 1997), aliphatic sulphur (Bartzatt and Carr, 1986), amino acids (Sharma and Bielski, 1991), carboxylic compounds (Bielski et al., 1994), organic nitrogen compounds (Carr and Erickson, 1988), phenol and its related compounds (Rush et al., 1995; Graham et al., 2004), recalcitrant organics (Gulyas, 1997) and thiourea (Sharma et al., 1999) were reported to be
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degraded by ferrate(VI). The percentage oxidation of these pollutants strongly depend on the
dose of ferrate(VI); and overdoses of ferrate(VI) were proved to be most effective in reducing
the organic concentration (Jiang and Lloyd, 2002). In a case study (Waite & Gilbert, 1978),
the maximum oxidation percentages with ferrate(VI) at pH < 8.0 were 18–47, 23–47, 85–100
and 32–55% towards oxidizing the benzene, chlorobenzene, allylbenzene and phenol,
respectively. The maximum oxidation efficiency was achieved when the molar ratios of the
ferrate to organic impurities were in the range of 3:1–5:1.

Literature survey reveals that ferrate(VI) oxidizes various synthetic organic
compounds, viz., benzene, chlorobenzene, allylbenzene and phenol, etc. (Bielski et al., 1994;
Gilbert, 1975; Waite, 1978). Ferrate(VI) degrades effectively the nitrogen-containing,
sulphur-containing compounds and several other organic compounds (De Luca et al., 1983;
Jiang and Lloyd, 2002; Sharma, 2002). Several reports indicated the oxidation of organic
compounds, viz., cystiene (Read et al., 2000), 2-mercaptoethansulphonate (Read et al., 1998),
thiourea (Sharma et al., 1999a), benzenesulphonate (Johnson and Read, 1996), 1,4-thioxane
(Read et al., 1998), aniline (Sharma et al., 2002), benzylamine (Hornstein, 1999),
glycoaldehyde, formaldehyde, formic acid, methanol (Carr et al., 1985), p-toluidine (Sharma
et al., 2002), etc. The degradation of these compounds with ferrate(VI) was reported to be
relatively fast and the increase of ferrate(VI) dose favored the decomposition of these
compounds. The reaction mechanism proposed with ferrate(VI) was one-electron and two-
electron transfer reactions to be associated with the degradation process for these organics.

Bielski and Thomas (1987) first proposed the one electron reduction of ferrate(VI) to
ferrate(V) by its reaction with hydrated electron (e_{aq}), (reaction (1.8)). Further, studies
showed that ferrate(VI) could be reduced to ferrate(V) through one electron transfer by its
reaction to organic radical compounds, which was well-known one-electron reductants
(reaction (1.9)) and reaffirmed with their pulse radiolysis and fast spectroscopic results
Introduction

\[ \text{FeO}_4^{2-} + e_{aq}^{-} \rightarrow \text{FeO}_4^{3-} \]  
\[ \text{FeO}_4^{2-} + R\text{COH} \rightarrow H\text{FeO}_4^{2-} + \text{RCO} \]  
\( \text{\ldots (1.8)} \)

Similarly, the reaction of phenol with ferrate(VI) was demonstrated with the phenoxy radical formation through hydrogen abstraction pathway (one-electron transfer), based on their reaction products analysis (Rush and Bielski, 1995). It was further, supported by the EPR studies, showed that the oxidation of phenol by ferrate(VI) proceeded through an intermediate radical species which was presumed as phenoxy radical (reaction (1.10)) (Huang et al., 2001).

\[ \text{OH}^- + \text{FeO}_4^{2-} \rightarrow \text{[Phenol]} \rightarrow \text{[Phenoxy radical]} + \text{FeO}_4^{2-} \]  
\( \text{\ldots (1.10)} \)

Further, the two-electron transfer mechanism of ferrate(VI) was proposed for the degradation of several nitrogen containing compounds (Johnson and Hornstein, 1994; 1996 & 2003). The oxidation of hydroxylamine was suggested to occur by concerted two hydrogen abstraction mechanism via the adduct formation between Fe and N atom of both reactants (reaction (1.11)). This argument was based on their several experimental results, including the stoichiometric, kinetic and products analysis of the reaction. The results of one-electron, viz., ascorbates, amino acids, esters, phenol, thiourea, thioacetamide etc. or two electron, viz., hydrazine, methylhydrazine, thiosulfate, benzene sulfinate, methionine, alcohols, thiol compounds, 1,4-thioxane, hydroxylamines, aniline etc. processes were compiled elsewhere (Lee et al., 2004).

\[ \text{NH}_2\text{OH} + \text{FeO}_4^{2-} \rightarrow \text{[Adduct]} \rightarrow \text{NOH} + \text{Fe(VI)} \]  
\( \text{\ldots (1.11)} \)

The degradation of several organic pollutants in aqueous solutions follows second order rate kinetics. The second order reaction rate constants obtained for these organic
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compounds are compiled elsewhere (Tiwari and Lee, 2011) which includes half-life period of the reactions at the specified pH. These results inferred that most of the studies were conducted at relatively higher pH condition where the ferrate(VI) was known to be stable. Moreover, the dominant species of the ferrate(VI) were the FeO$_4^{2-}$ and HFeO$_4^{-}$. The reaction rate constants were high enough, whereas the half-life period was relatively low (except few cases) suggested fast and effective degradation reaction occurred with ferrate(VI).

Ferrate(VI) possessed ability to oxidize emerging water contaminants like estrogens, bisphenol A, and pharmaceuticals present in water (Anquandah and Sharma, 2009; Lee et al., 2005; 2008 & 2009; Lee and Gunten, 2010; Li and Gao, 2009; Sharma et al., 2006a & 2006b; 2008a & 2008b; 2009a & 2009b). Several sulphur containing antibiotics including sulfamethoxazole, sulfametazine, sulfamethizole, sulfadimethoxine, sulfasoxazole etc. were treated with ferrate(VI) and rate expressions were obtained. It was reported that 1:1 stoichiometry occurred in the degradation of these drugs with ferrate(VI) and rate law for each reactant was found to be pseudo-first-order studied with an excess dose of ferrate(VI) (Sharma et al., 2006b; Sharma, 2008). Similarly, the phenolic endocrine-disrupting chemicals (EDCs) and phenols were effectively oxidized by ferrate (VI) as studied for natural and waste water samples (Lee et al., 2005). The degradation of estrone (E1), 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) was conducted with varied ferrate(VI) doses and solution pH. It was demonstrated that at pH 9.0 the maximum degradation of these compounds was achieved and a complete degradation of these pollutants were occurred with Ca. three times of ferrate(VI) dose (Jiang et al., 2005). Similarly, ferrate(VI) was found to be superior oxidant than usual electrochemical reduction of bisphenol A, E2 and 4-tert-octylphenol (Lee et al., 2005). The kinetic model and path of degradation process for five different EDCs viz., BPA (Bisphenol A), EE2 (17α-ethynylestradiol), E1 (Estrone), E2 (β-estradiol) and E3 (Estriol) were studied using the LC/MS and GC/MS spectroscopic methods; the obtained result suggested that protonated species of ferrate(VI) i.e., HFeO$_4^{-}$ was found to possess an enhanced oxidative
property than non-protonated species FeO₄²⁻ toward all these EDCs studied, however, the
dissociated (ionized) EDCs were more reactive towards the protonated ferrate(VI) (Li et al.,
2008).

Ferrate(VI) showed an useful oxidizing agent toward the degradation of several
inorganic water pollutants, viz., superoxide ion, hydrogen peroxide (Rush et al., 1996),
hydrazine (Johnson and Honstein, 1994), hydroxylamine (Johnson and Hornstein, 2003),
cyanide (Sharma et al., 1998b), ammonia (Sharma et al., 1998a) etc. The mechanism of
oxidation of inorganic compounds with ferrate(VI) was suggested to be one and two-electron
processes. Compounds like iodides, cyanides, sulfite etc. demonstrated to be one electron
process whereas, the oxy compounds of arsenic, selenium, nitrogen and sulphur were
possessed with two-electron mechanism while these were reacted/degraded with ferrate(VI).
The reactions of ferrate(VI) with a series of inorganic compounds, such as iodide, cyanide,
superoxide, sulfide, hydrazine, ammonia, azide and oxy-compounds of nitrogen, sulphur,
selenium and arsenite, possessed with seconds-order kinetics (Carr, 2008; Johnson and
Hornstein, 1994 & 2003; Johnson and Read, 1996; Johnson et al., 2008; Johnson and Sharma,
1999; Sharma, 2002 & 2010a; Sharma et al., 1997; 2002 & 2005b; Lee et al., 2003). In
general, similar to the organic compounds the reaction with inorganic compounds (P) was
demonstrated as equation (1.12):

\[- \frac{d[Fe(VI)]}{dt} = kp[Fe(VI)][P] \]  \( … (1.12) \]

where \( k_P \) is the second-order rate constant for the reaction. It was found that the
reactions of ferrate(VI) with cadmium(II)cyanide (Cd(CN)₄²⁻), zinc(II)cyanide (Zn(CN)₄²⁻),
and selenite (SeO₃²⁻) showed the following rate equations (1.13 and 1.14) (Johnson and
Bernard, 1992; Yngard et al., 2008; Yngard et al., 2007). The order of half was found with
respect to the concentrations of Cd(II) and Zn(II) cyanides (equation (1.13)). This was
different from the second-order rate law observed for the reaction of ferrate(VI) with other
The reaction of ferrate(VI) and selenite possessed with first and second-order selenite concentrations dependence terms in the rate law (equation (3.7)) (Johnson and Bernard, 1992).

\[ -\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)][SeO_\text{3}^{2-}] + k_2[Fe(VI)][SeO_\text{3}^{2-}] \] ... (1.14)

where \( k_2 \) is the third order rate constant.

The rate constants and also the stocchiometry and the products obtained for various inorganic compounds were compiled elsewhere (Sharma, 2010a & 2010b; Tiwari and Lee, 2011). Similarly, the degradation of thiourea and thioacetamide was studied (Sharma et al., 1999a) and it was proposed that thiourea and thioacetamide were converted into sulphate at pH 9.0 using ferrate(VI). The stoichiometric ratios of ferrate(VI) and thiourea and thioacetamide was found to be 1:0.38±0.02. Moreover, the proposed reaction was suggested as equations (1.15) and (1.16).

\[ 8\text{HFeO}_4^- + 3\text{NH}_2\text{CSNH}_2 + 9\text{H}_2\text{O} \rightarrow 8\text{Fe(OH)}_3 + 3\text{NH}_2\text{CONH}_2 + 3\text{SO}_4^{2-} + 2\text{OH}^- \] ... (1.15)

\[ 8\text{HFeO}_4^- + 3\text{CH}_3\text{CSNH}_2 + 9\text{H}_2\text{O} \rightarrow 8\text{Fe(OH)}_3 + 3\text{CH}_3\text{CONH}_2 + 3\text{SO}_4^{2-} + 2\text{OH}^- \] ... (1.16)

Ferrate(VI) can achieve disinfection at relatively low dosages over wide range of pH (Cho et al., 2006; Jiang et al., 2007; Sharma, 2007). The disinfection property of ferrate(VI) was first optimized to kill two pure laboratory cultures of bacteria, Non-recombinant Pseudomonas and Recombinant Pseudomonas (Murmann and Robinson, 1974). At a dose of 0-50 mg/L as FeO_4^{2-}, the bacteria were removed completely. The oxidation of E. Coli DNA polymerase-I by ferrate(VI) resulted in loss of polymerization and 3-5 exonuclease activity and thus the irreversible inactivation of the enzyme was reported (Basu et al., 1987). Moreover, the reactivity of deoxyribonucleosides by ferrate(VI) was cuased DNA chain cleavage through a mechanism in which base loss was followed by β-elimination at the basic
Introduction

The results suggested irreversible inactivation of *E. Coli* by ferrate(VI). The ferrate(VI) showed sufficient disinfection capability as to kill the *Escherichia coli* (*E. coli*). At pH 8.2 with a dose of 6 mg/L as Fe, the *E. coli* percentage kill was 99.9% but when the contact time was extended to 18 min even with the reduced dose 2.4 mg/L as Fe facilitated the complete removal of *E. coli* (Gilbert *et al.*, 1976). The results also demonstrated that the disinfecting ability of FeO$_4^{2-}$ was increased markedly if water pH was below 8.0. Similarly, the secondary effluent disinfection study showed 99.9% of total *coli forms* and 97% of the total viable bacteria were removed at a dose of 8 mg/L of ferrate(VI) (Waite, 1979). The real sewage wastewater and a model water *E. coli* (concentration 3.2x10$^8$ /100 mL) were used to assess the ferrate(VI) capability as coagulant behavior (compared to ferric and aluminum sulfate) for real wastewater and disinfection for the model *E.coli* water (compared with sodium hypochlorite) (Jiang *et al.*, 2007). The ferrate(VI) showed significantly better performance over ferric and aluminum sulphate. Moreover, the disinfection towards *E. coli* was also comparatively better than hypochlorite. In a line the comparative performance of ferrate(VI) with ferric sulfate and aluminum sulfate were carried out. Further the results indicated that ferrate(VI) possessed better suitability over the ferric and aluminium sulphate (Jiang *et al.*, 2006). Other reports indicated that ferrate(VI) was much effective to kill *Eschericha coli* (*E. coli*) (Murmann and Robinson, 1974) and total *coli forms*. Moreover, it was reported that ferrate(VI) can rapidly inactivate the *f2 Coliphage* at low concentrations; 99% of *f2 Coliphage* was inactivated at 1 mg/L of ferrate(VI) in 5.7 min at pH 6.9 and only 0.77 min at pH 5.9. A higher dose 10 mg/L of ferrate(VI) was required in order to achieve 99.9% inactivation at pH 7.8 with a contact time 30 min (Schink and Waite, 1980; Jiang, 2007). Disinfection tests of sodium ferrate(VI) on spore-forming bacteria also demonstrated that aerobic spore-formers were reduced up to 3-log units while sulfite-reducing *clostridia* were effectively killed by ferrate(VI) (White and Franklin, 1998). Both bacteria were resistant to chlorination process. Ferrate(VI) also inhibited the respiration of the
bacterium *Sphaerotilus*; suggesting potential role in treating sludge for disinfections. The use of ferrate(VI) was discussed for the treatment of wastewaters particularly its disinfection property and reported that it can reduce 50% more color (Vis400-abs), 30% more COD, and kill 10% more bacteria in wastewater as compared to aluminium sulphate and ferric sulphate (Jiang and Panagoulopoulos, 2004).

Ferrate(VI) was demonstrated to possess fairly good coagulation/flocculation properties, and hence able to coagulate non-degradable impurities particularly the heavy metal toxic ions or radio nuclides. Moreover, the Fe(III) as iron(III) hydroxides are known to be a potential adsorbent, possibly can remove the free metallic impurities even by adsorption process. The arsenic(III) oxidized to As(V) and hence, the removal of As(V) by reduced Fe(III) via coagulation process was effectively achieved (Lee *et al.*, 2003). The two moles of ferrate(VI) required to oxidize three moles of As(III) (reaction 2.9). The oxidation of As(III) followed second order rate law at pH 8.4 to 9.0. It was noted that a complete oxidation took place within a second.

\[
2\text{Fe(VI)} + 3\text{As(III)} \rightarrow 2\text{Fe(III)} + 3\text{As(V)} \tag{1.17}
\]

Further, it was demonstrated that even at smaller dose of ferrate(VI) along with the supplementary dose of Fe(III) may achieve the efficiency to remove the arsenic from the arsenic contaminated river water (Nakdong River, Korea). Potassium ferrate(VI) was a potential chemical to remove several metal cations/anions including Mn\(^{2+}\), Cu\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Cr\(^{3+}\) and Hg\(^{2+}\) from aqueous solutions via coagulation/adsorption process using lower dose of ferrate(VI) 10-100 mg/L (Bartzatt *et al.*, 1992). Interestingly, the americium and plutonium radio nuclides were treated with ferrate(VI) at pH 11.5-12.0 and results showed that the treated water samples possessed significantly less radioactivity (Potts *et al.*, 1994). This was assumed that these radio nuclides were coagulated with reduced Fe(III). Similarly, other radio nuclides were treated with ferrate(VI) and showed that ferrate(VI) could play a wider possible role in radioactive waste management studies (Midkiff *et al.*, 1995; Stupin and
Recently, the removal of As(III) by ferrate(VI), ferrate(VI)/Fe(III) and ferrate(VI)/Al(III) salts was studied as a function of pH (8.0 to 6.0) and anion concentration (Jane et al., 2009). Removal of As(III) was increased with decrease in pH from 8 to 6. It was suggested that phosphate and silicate were forming the inner-sphere complexes and compete strongly with arsenic for Fe or Al oxy/hydroxide surfaces and such competition exist only at higher concentrations of phosphate and silicate, causing an apparent decrease in removal efficiency of arsenic from the system. Bicarbonate also influenced the removal of As(III), but much higher levels were needed than that of phosphate and silicate (Jane et al., 2009). Ferrate(VI) was advantageous in coagulation where it was applied in a preoxidation step of the treatment (Ma and Liu, 2002a & 2002b; Ma et al., 2008a & 2008b). In the preoxidation process, ferrate(VI) destroyed the organic coating on the particle and thus aids in the coagulation process (Liu and Liang, 2008). Enhanced coagulation of metals and algae were achieved when water was pretreated with ferrate(VI) (Ma and Liu, 2002a; Ma et al., 2008a & 2008b; Tien et al., 2008). Interestingly, removal of arsenic and fulvic acid were more effective with the combination of ferrate(VI) and poly aluminium chloride or ferric chloride (Jain et al., 2009; Lee et al., 2003; Qu et al., 2003; Sharma and Sohn, 2009; Sharma et al., 2007).

Similarly, the metal complexed species were studied and discussed previously particularly the metal(II) cyanide complexes (Johnson and Sharma, 1999; Sharma et al., 2005b; Yngard et al., 2007 & 2008). An interesting study using Cu(II) and Ni(II) cyanide complexes were carried out and showed that a complete degradation of cyanide along with the complete removal of free copper and partial removal of nickel was achieved from the ferrate(VI) treated samples (Lee and Tiwari, 2009). Further the study was extended to employ it for the treatment of real electroplating wastes containing the copper and nickel complexed cyanides (Tiwari et al., 2007). Recent studies again reported the efficiency of ferrate(VI) for treating the mixed systems containing the organic ligand species with heavy metal toxic ions.
Decomplexation of Cu(II)-EDTA system by ferrate(VI) was studied by Tiwari et al., (2008). It was reported that the acidic conditions favor the decomplexation of Cu(II)-EDTA as the decomplexation was almost 100% up to pH 6.5, while it was only 35% at pH 9.9, as the species of ferrate(VI), such as HFeO$_4^-$ and H$_2$FeO$_4$, which are relatively more reactive than the unprotonated species FeO$_4^{2-}$; which were predominant species below neutral pH. However, the removal of total Cu(II) was rapid at higher pH values, which could be explicable due to the reason that at lower pH values the adsorption/coagulation capacity of Fe(III) is greatly retarded. The kinetic study further revealed that the data was reasonably fitted well to the second order rate reaction than the first order rate reaction in an excess of ferrate(VI) concentration. Similarly, in the case of Zn(II)-NTA system, the decomplexation by ferrate(VI) showed second order rate kinetics and the rate constant value was found to be 8.80x10$^{-1}$ M$^{-1}$s$^{-1}$. Further, the reaction was almost unaffected in presence of 1000 times NaNO$_3$, NaCl and NaClO$_4$. However, it was greatly suppressed in presence of Na$_2$SO$_3$ and NaNO$_2$ electrolyte. This suggested that ferrate(VI) was preferred to the oxidation of SO$_3^{2-}$ and NO$_2^-$ rather the Zn(II)-NTA complex (Yang et al., 2010). Removal of Cd(II)-NTA by ferrate(VI) was investigated with variation of solution pH from 8 to 12 (Yu et al., 2012). At pH 8, a rapid ferrate(VI) reduction was observed in initial reaction time but much reduced ferrate(VI) reduction was noticed at higher solution pH. Total cadmium removal increased as the solution pH lowered down. However it was below 5% for all solution pH. The reduced decomplexation of Cd(II)-NTA at higher solution pH was due to the little mineralization of NTA to simple inorganic products such as ammonia, nitrate and carbon dioxide. TOC data showed that maximum 23% of NTA was degraded. ICP data also indicated that increasing the dosages of ferrate(VI) from 1.0x10$^{-4}$ mol/L to 2.0x10$^{-4}$ mol/L apparently caused an increase in the removal of Cd(II) respectively from 14.9 to 23.8%. The studies also indicated that very fast removal of cadmium by ferrate(VI) occurred as within few minutes of contact time, maximum cadmium was removed.
**Introduction**

Ferrate(VI) was employed in the treatment of simulated wastewaters contaminated with the M(II)-complexed species viz., Cd(II)-IDA and Ni(II)-IDA. The batch reactor operations shows that a fast and efficient decomplexation/removal of Cd(II)/or Zn(II)-IDA was obtained for various molar concentrations (0.3–10.0 mmol/L) of the complex species treated with a constant dose of ferrate(VI) (i.e., 1.0 mmol/L). The efficiency of the ferrate(VI) was increased further decreasing the solution pH from 10.0 to 8.0. The removal of metals was further enhanced raising the pH of the ferrate(VI) treated samples to 12.0 and almost 100% of Cd(II) was removed (Tiwari et al., 2014). The ferrate(VI) treatment of wastewaters contaminated with metal(II)-complex species viz., copper(II)-NTA; copper(II)-EDTA and cadmium(II)-EDTA was also found that ferrate(VI) possesses multifunctional application in wastewater treatment as it oxidizes the degradable impurities and removes metallic impurities by coagulation process (Sailo et al., 2015).

Endocrine disrupting chemicals and drugs related compounds were of current research interest owing to its concern towards adverse environmental concerns. Pioneer studies using ferrate(VI) for the degradation of EDCs were carried out elsewhere (Hu et al., 2004; Jiang et al., 2005; Lee et al., 2005; Sharma et al., 2006). The oxidation of estrone (E1), 17β-estradiol (E2), and 17α-ethynylestradiol (EE2) by potassium ferrate(VI) was studied as a function of pH and dosages. The results suggested that pH 9 was the most favorable condition to obtain the highest removal efficiency and the complete removal was obtained at a molar ratio of ferrate(VI) to estrogens >3:1 in water samples. Jiang et al., (2005) showed that in comparison with electrochemical oxidation, ferrate(VI) could reduce much more bisphenol A, E2 and 4-tert-octylphenol. The effectiveness of ferrate(VI) for the oxidative removal of phenolic EDCs was also confirmed in both natural water and wastewater samples (Lee et al., 2005). The apparent second-order rate constants for the reaction of ferrate(VI) with the selected EDCs (E2, EE2, and bisphenol A) was ranged from 6.4×102 to 7.7×10² M⁻¹ s⁻¹ at pH 7.
Among the prominent endocrine disrupting chemicals of environmental significance, two synthetic EDCs: bisphenol A (BPA) and 17α-ethynylestradiol (EE2), and three natural EDCs: estrone (E1), 17β-estradiol (E2), and estriol (E3) were investigated and quantified their reaction kinetics with ferrate(VI). BPA was degraded completely degraded in less than 5 minutes using the ferrate(VI) dose five times to the BPA. Moreover, the degree of organic mineralization was significantly less than 100%, indicating the presence of reaction intermediate products which persist well beyond the disappearance of the BPA (Li et al., (2007)). Hence, keeping in view the present study is an extension of several studies towards the treatment of several micro-pollutants from aquatic environment using ferrate(VI), as an efficient alternative oxidant. The study is extended for various parametric studies viz., the effect of pollutant concentration and solution pH as to deduce the mechanism involved in the ferrate(VI) oxidative degradation of EDCs. Further, the kinetics of the degradation of EDCs by ferrate(VI) was obtained in order to optimize the degradation efficiency of these EDCs by ferrate(VI) from aqueous solutions. The TOC measurement was enabled to predict an overall mineralization of these EDCs from aqueous solutions and presence of several electrolyte concentrations provided to simulate the study for the real water matrix treatment contaminated with these EDCs by ferrate(VI).

1.6. SCOPE OF THE PRESENT INVESTIGATION

Water resources are continually and increasingly contaminated with domestic as well as industrial effluents. Introducing the chemical pollutants in water, particularly a variety of micro-pollutants including EDCs, pharmaceuticals and personal care products etc. are becoming more and more problematic due to its persistency/toxicity in aquatic environment. Endocrine disrupting chemicals (EDC) are one of the main focuses of the current environment research, as it may cause for several adverse health effects in an intact organism, or its progeny, subsequent to endocrine malfunction (Zhang and Zhou, 2005). EDCs are a wide
Introduction

A variety of both natural and man-made chemicals which typically exert effects, either directly or indirectly, through receptor-mediated processes mimicking endogenous hormones by inhibiting the normal hormonal activities (Roepka et al., 2005). They disrupt endocrine and other vital systems in aquatic organisms (Lange et al., 2001; Kidd et al., 2007) and increases the risk of cancer (Benhamou and Saras, 2002; Kang and Lee, 2005; Notch et al., 2007) even at nanogram levels. Concentrations as low as 0.1 ng/L of an estrogen are sufficient for significant estrogenic effects (Aerni et al., 2004). The presence of EDCs in water bodies and sediments was attributed primarily due to human and animal excretions and their incomplete removal from the sewage treatment plants (Filali-Meknassi et al., 2004). Low efficiencies of estrogen removal are observed in many conventional activated sludge systems which operate with relatively short sludge retention times (SRTs). Conventional treatment plants are not designed to remove trace EDCs and many of these conjugates are cleaved to free estrogens through microbial processes before or during sewage treatment. Residues of EDCs in the secondary effluents may pose either acute or chronic adverse effects on the aquatic organisms in receiving water, and on humans if the reclaimed water is returned to the water supply (Nakada et al., 2007).

Oxidation/disinfection and coagulation are two important unit processes for water treatment. A wide range of coagulants and oxidants are employed in water and wastewater treatment. The most common coagulants used include ferric sulphate, aluminium sulphate and ferric chloride and the oxidants/disinfectants used are halogen based oxidants such as chlorine, chlorine dioxide and sodium hypochlorite, and oxygen based oxidants such as ozone and hydrogen peroxide. Coagulation destabilizes colloidal impurities and transfer small particles into large aggregates, which then be removed by sedimentation and filtration. Oxidants are applied for the oxidative removal of chemical pollutants and control of pathogenic microorganisms in water and wastewater. Although extensive use of these chemicals have showed its limitations because of its environmental concern as due to the
formation of toxic disinfection byproducts, excessive sludge and on site odour. These limitations combined with the increasing levels of water pollution, clean water shortages and more stringent regulatory standards of drinking water and wastewater have led to the search of more effective, viable and environmentally benign oxidant and coagulant.

Certainly the existing water and wastewater treatment plants have been designed for the best in treatment and removal of contaminants, especially those which are specified in the existing regulations. However, the occurrence of the new emerging micro-contaminants such as EDCs which possesses a wide range of chemical properties, the success in their removal varies greatly upon their specific properties and thus requires effective treatment. A number of technologies are available with varying degree of success to control these pollutions. However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control.

The existing water treatment technology is not sufficient to treat these complex contaminants. To reduce the potential risk caused by EDCs in treated wastewater discharged to aquatic environments, their removal is considered to be significantly important. Ferrate(VI) is a promising ideal substitute over other oxidants often employed in wastewater treatment methods due to its strong oxidizing capacity, efficiency in disinfection and coagulation as well as its environmentally benign nature. In fact, ferrate(VI) was repeatedly demonstrated to be very effective treatment chemical in all sorts of water and wastewater systems. The redox potential of the couple ferrate(VI)/Fe(III) \([E^0 (\text{FeO}_4^{2-}/\text{Fe}^{3+}) \text{ and } E^0 (\text{FeO}_4^{2-}/\text{Fe(OH)}_3)]\) are found to be 2.20 V and 0.72 V, respectively at pH 1 and 14. These values are significantly higher than those corresponding to the commonly used oxidants \(\text{viz.}, \text{Mn(VII)/Mn(IV)}\) \(E^0 = 1.679 \text{ V}\) and \(0.588 \text{ V}\) and \(\text{Cr(VI)/Cr(III)}\) \(E^0 = 1.33 \text{ V}\) and \(-0.12 \text{ V}\) respectively found at pH 1 and 14.

Further, the by-products formed with the reduction of ferrate(VI) i.e., Fe(III) as in the form of \(\text{Fe(OH)}_3\), is reported to be fairly good coagulant/flocculent and adsorbent. Hence, we may conclude that the application of ferrate(VI) in the treatment of waste waters replaces the
commonly used oxidants in the pre-stage and in the latter stage it may replace the coagulant/flocculent/adsorbent used to remove the colloidal or suspended impurities including the heavy metal toxic ions. Hence, we underline the role of ferrate as multifunctional in the treatment of waste/effluent waters. Moreover, the by-products formed, i.e., ferric hydroxide, are reported to be non-toxic and be separated easily from the water matrix by simple sedimentation process. This exaggerates the use of ferrate in such purposes. In other words, ferrate is an environment friendly oxidant that represents a viable substitute over other oxidants, particularly chromate permanganate or chlorine, which are of environmental concern. Therefore, ferrate(VI) is an "environmentally safe" oxidant and may be termed as ‘Green Chemical’ (Tiwari et al., 2005; Yang et al., 2010).

The role of Ferrate(VI) in wastewater treatment offered a vast scope as ferrate(VI) was rendered as one of efficient oxidant, disinfectant, flocculent, coagulant. Therefore, it is known to be a promising multi-purpose and environmental friendly water treatment chemical. Although a number of research studies have shown that ferrate(VI) is very effective in the removal/degradation of various waste water contaminants however, only scanty of work was carried out as to explore its possible application in the treatment/degradation of various kind of endocrine disrupting chemicals. Therefore, the proposed study is to enhance the knowledge towards the applicability of ferrate(VI) in water treatment technology particularly the degradation of EDCs viz., bisphenol A (BPA), diclofenac sodium salt (DFS), 17α-ethynylestradiol (EE2), 4-tertoctylphenol and potassium phthalate from the aqueous solutions under different parametric studies which could helped in scaling up the laboratory data to pilot or large scale treatment of contaminated water. The mineralization of these EDCs provides to achieve an ultimate goal of complete degradation of EDCs from aqueous solutions. Additionally, the presence of several species simulates the treatment studies for real water matrix treatment or potential of ferrate(VI) towards these water contaminats.