FERRATE(VI) : A GREEN CHEMICAL IN THE TREATMENT OF WASTEWATER CONTAMINATED WITH SOME ENDOCRINE DISRUPTING CHEMICALS (EDCs)

A Thesis submitted
in partial fulfilment of the requirements for the Degree of

Doctor of Philosophy
in
Chemistry

By

LALSAIMAWIA SAILO

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CERTIFICATE

This is to certify that the thesis entitled, ***'Ferrate (VI): A green chemical in the treatment of wastewater contaminated with some endocrine disrupting chemicals (EDCs),'*** submitted by ***Mr. Lalsaimawia Sailo,*** for the degree of ***Doctor of Philosophy*** in the Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D degree. This work has not been submitted for any in any other university.

Dated: March 12, 2016

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DECLARATION OF THE CANDIDATE

MIZORAM UNIVERSITY
November, 2015

I Lalsaimawia Sailo, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to do the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

This is being submitted to the Mizoram University for the degree of Doctor of Philosophy in Chemistry.

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(Prof. DIWAKAR TIWARI)
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I dedicate this thesis to my beloved aunty, *Lallliannguri Sailo* (1956-2011), who had always been for me to to fully accomplish my career.

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(LALSAIMAWIA SAILO)

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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 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 contaminants. 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 H_2S 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 H_2S 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 *et al.*, 2009). EDCs have been attributed to distube 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). Therfore, the low level prresece 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)

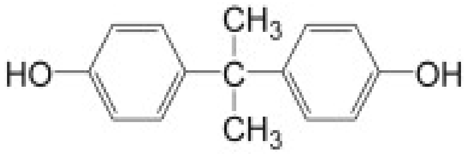


Figure 1.1. Structure of Bisphenol A (BPA).

Bisphenol A has become ubiquitous in the environment for 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 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 testosterone levels (Nieminen *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)

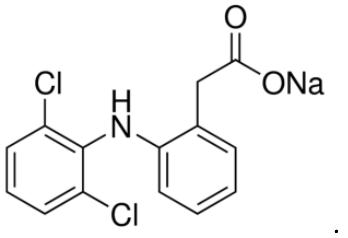


Figure 1.2. Structure of diclofenac sodium salt (DFS).

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 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 marine phytoplankton *Dunaliella tertiolecta* for concentrations of 25 mg/L and above. For this organism, 96 h EC_{50} of 185.69 mg/L was found (DeLorenzo and Fleming, 2008).

1.1.3. 17α-ETHYNYLESTRADIOL (EE2)

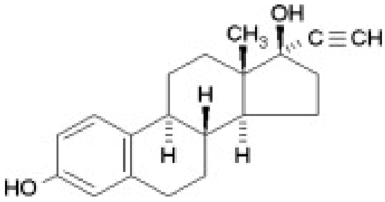


Figure 1.3. Structure of 17α-ethynylestradiol (EE2).

17α-ethynylestradiol, also known as EE2 (19-nor-17α-pregna-1,3,5(10)-trien-20-yne-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® 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 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).

Similalry, 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; Dzieweczynski 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)

(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 greately 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-TERT-OCTYLPHENOL

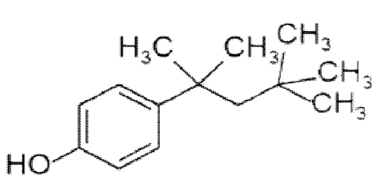


Figure 1.4. Structure of 4-tert-octylphenol.

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 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 ($\log K_{OW}$) value suggested assuming the contaminant tends to bind to 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

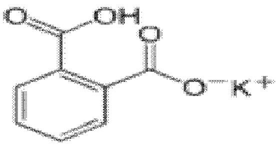


Figure 1.5. Structure of potassium phthalate.

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; Mallevialle *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) 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 ($E^o = 2.07$ 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 S^{2-}, to form oxyanions such as SO_3^{2-} and SO_4^{2-}. 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 *Cryptosporidum* 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 ·OH radicals is commonly accelerated by combining ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), heterogeneous photocatalysis, UV radiation, ultrasound, and (or) high electron beam irradiation. Of these, O_3–H_2O_2, O_3–UV, H_2O_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_2O_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_2O_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_2O_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_2O_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_2O_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, 1982*a* &1982*b*, 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, 1982*b*), and pesticides (Beltrán *et al.,* 1994*a*, 1994*b*). 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_2O_2 and H_2O_2–UV processes in most cases.

Hydrogen peroxide – Ultraviolet

Under UV irradiation, H_2O_2 will be photocatalyzed to form two hydroxyl radicals. The formed hydroxyl radicals then react with organic contaminants or undergo an H_2O_2 decomposition–formation cycle (Crittenden *et al.,* 1999). Unlike ozone, H_2O_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_2O_2, such direct photo-oxidation would be expected to have a major contribution to the overall degradation in the H_2O_2–UV system. Like the O_3–UV process, the H_2O_2–UV process is mainly used for the oxidation of refractory contaminants. For example, Beltrán *et al.* (1993) studied the H_2O_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_2O_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

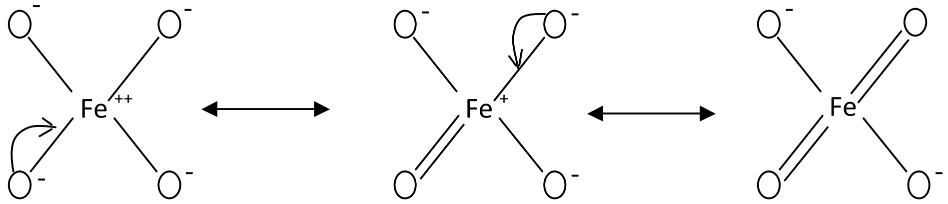
The oxidation system based on the Fenton's reagent (hydrogen peroxide in presence of a ferrous salt) is used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, 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_2FeO_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 electro-chemical methods. Of the several ferrate(VI) salts prepared, K_2FeO_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_2FeO_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.



1 2 3

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).

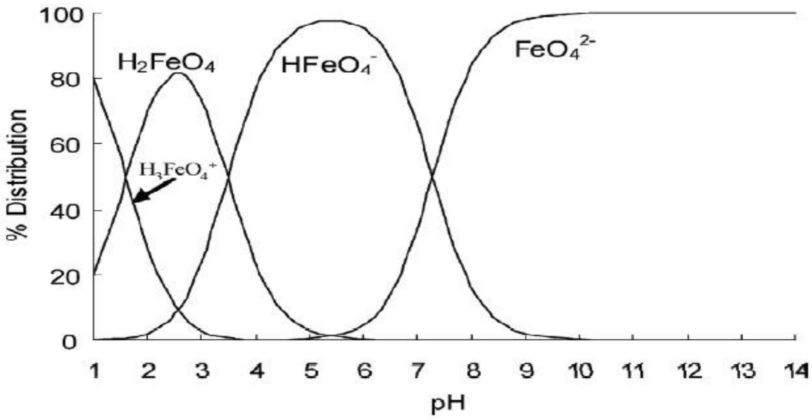


Figure 1.7. Species distribution of ferrate(VI) in aqueous solution (Tiwari *et al.*, 2007)

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).

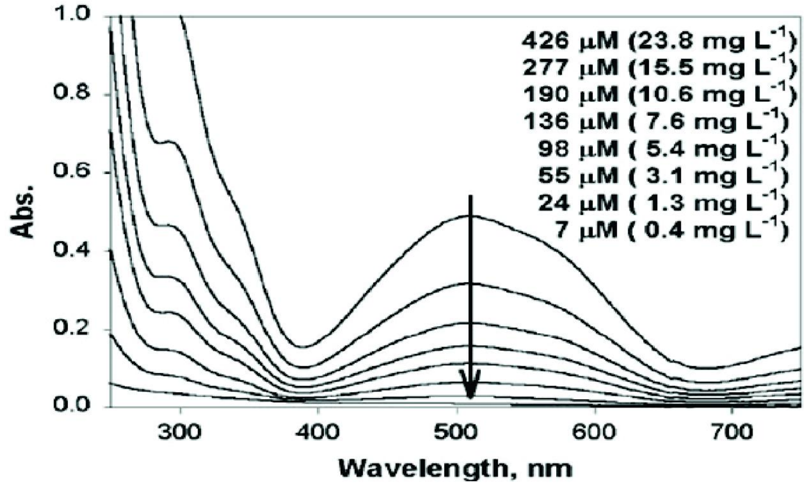


Figure 1.8. UV-Vis absorption spectrum of ferrate(VI) in aqueous solution as a function of its concentration, pH = 9.2, 25 mM phosphate buffer (Lee *et al.*, 2004)

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 ^{0}C (Wagner *et al.*, 1952). The stability of K_2FeO_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 $K_2Zn(OH)_4$, KIO_4, $K_2B_4O_9$, K_3PO_4, $Na_2P_2O_7$, Na_2SiF_6, Na_2SiO_3, Na_2MoO_4 and Na_2WO_4 have no effect on the stability of K_2FeO_4 (Stuart and Ghosh, 1999). A 0.5 M K_2FeO_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 K_2FeO_4 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.

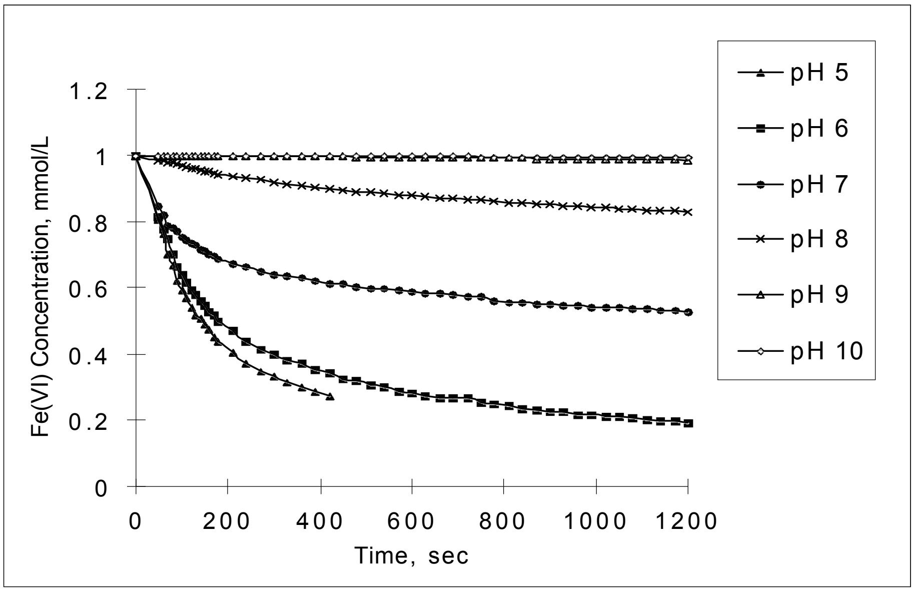


Figure 1.9. The change of the ferrate(VI) concentration as a function of time at various pH values[Initial concentration of ferrate(VI): 1 mM] (Tiwari et al,. 2007)

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).

$$4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 8KOH + 3O_2 \qquad \ldots (1.1)$$

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).*

$2H_3FeO_4^{+} \leftrightarrow [H_4Fe_2O_7]^{2+} + H_2O \quad k_2 = 3.5x10^{5}\ M^{-1}\ s^{-1}$ … (1.2)

$[H_4Fe_2O_7]^{2+} + 2H^{+} + 6H_2O \rightarrow Fe_2(OH)_2(H_2O)_8^{4+} + 3/2\ O_2$ Fast step … (1.3)

$H_3FeO^{4+} + H_2FeO_4 \leftrightarrow$ [diferrate] $\quad k_4 \approx 3.5x105\ M^{-1}\ s^{-1}$ … (1.4)

$2H_2FeO_4 \leftrightarrow$ [diferrate] $\quad k_5 = 1.5x104\ M^{-1}\ s^{-1}$ … (1.5)

$H_2FeO_4 + HFeO^{4-} \leftrightarrow$ [diferrate] $\quad k_6 \approx 1.5x104\ M^{-1}\ s^{-1}$ … (1.6)

$2HFeO^{4-} \leftrightarrow [Fe_2O_7]^{2-} + H_2O \quad k_7 = 2.5x102\ M^{-1}\ s^{-1}$ … (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).*

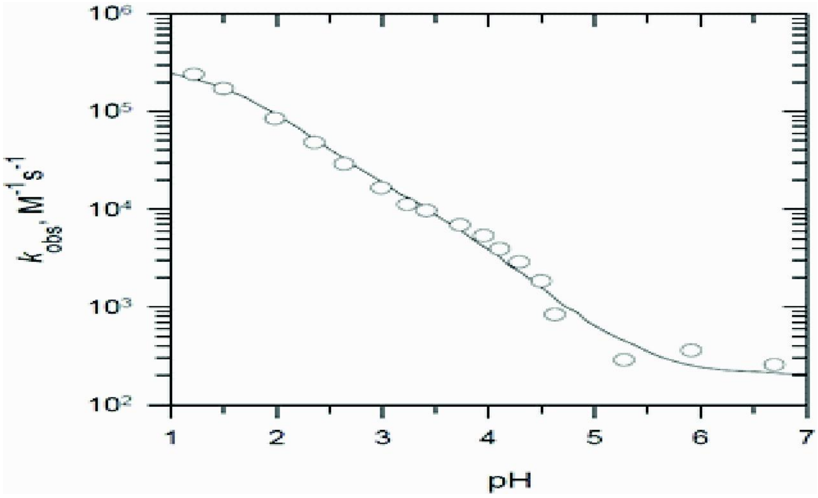


Figure 1.10. The second-order rate constants for the decay of ferrate(VI) to iron(III) in 5 mM (phosphate/acetate) buffers (Rush et al.,1996)

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 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 (FeO_4^{2-}/Fe^{3+}) and E^0 ($FeO_4^{2-}/Fe(OH)_3$ 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 *et al.,*1985; Rao *et al.,*1988; Delaude and Laslo,1996; Norcross *et al.*, 1997), carboxylic compounds (Bielski *et al.*, 1994), amino-acids (Sharma and Bielski, 1991; Rush and Bielski, 1993), phenol (Rush *et al.,*1995), 1,2-Diols (Rao *et al.,* 1991), organic nitrogen compounds (Carr *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 *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 72 (Anquandah and Sharma, 2009; Lee *et al.,* 2008; Lee *et al.,* 2009; Lee *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*

Oxidant	**Reaction**	**E^0, V**
Chlorine	$Cl_2(g) + 2e^- \leftrightarrow 2Cl^-$ $ClO^- + H_2O + 2e^- \leftrightarrow Cl^- + 2OH^-$	1.358 0.841
Hypochlorite	$HClO + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$	1.482
Chlorine dioxide	$ClO_2(aq) + e^- \leftrightarrow ClO_2^-$	0.954
Perchlorate	$ClO_4^- + 8H^+ + 8e^- \leftrightarrow Cl^- + 4H_2O$	1.389
Ozone	$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + 2H_2O$	2.076
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.776
Dissolved oxygen	$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1.229
Permanganate	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$ $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$	1.679 1.507
Chromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H2O$	1.33
Ferrate(VI)	$FeO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Fe^{3+} + 4H_2O$ $FeO_4^{2-} + 8H_2O + 3e^- \leftrightarrow Fe(OH)_3 + 8H_2O$	2.20 0.70

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).

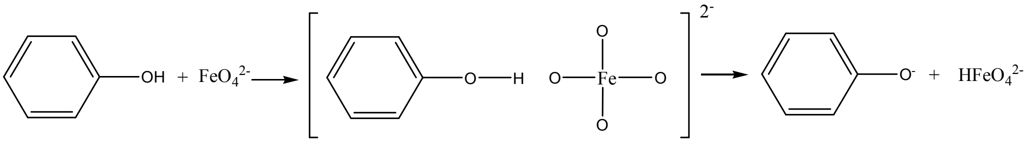
A range of organic contaminants were oxidized readily by ferrate(VI). Alcohol (Norcross *et al.*, 1997), aliphatic sulphur (Bartzatt and Carr, 1986), amino acids (Sharma and Bielski, 1991), carboxylic compounds (Bielski *et al.*, 1994), organic nitrogen compounds (Carr and Erickson, 1988), phenol and 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 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), benzenesulfonate (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 (Bielski, 1991 & 1992; Rush and Bielski, 1986).

$FeO_4^{2-} + e_{aq}^{-} \rightarrow FeO_4^{3-}$ … (1.8)

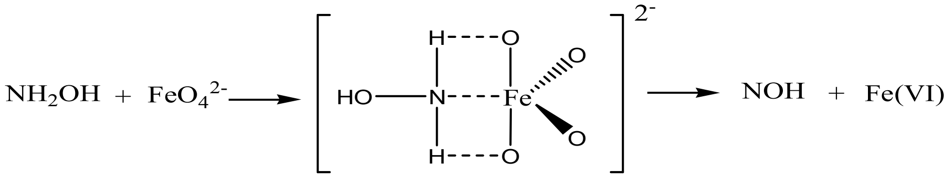
$FeO_4^{2-} + R\dot{C}OH \rightarrow HFeO_4^{2-} + RCO$ … (1.9)

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).



… (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).



… (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 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 FeO_4^{2-} 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):

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

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 ($Cd(CN)_4^{2-}$), zinc(II)cyanide ($Zn(CN)_4^{2-}$), and selenite (SeO_3^{2-}) 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 cyanides (CN^-, SCN^-, $Cu(CN)_4^{3-}$ and $Ni(CN)_3^-$) (Sharma *et al.,* 1998b; 2002 & 2005a; Yngard *et al.,* 2007).

$$-\frac{d[Fe(VI)]}{dt} = k_P[Fe(VI)][M(CN)_4^{2-}]^{0.5} \text{ where M= Cd(II), Zn(II)} \qquad \ldots (1.13)$$

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).

$$-\frac{d[Fe(VI)]}{dt} = k_P[Fe(VI)][SeO_3^{2-}] + k_2\,[Fe(VI)][SeO_3^{2-}]^2 \qquad \ldots (1.14)$$

where k_2 is the third order rate constant.

The rate constants and also the stocichiometry 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).

$$8HFeO_4^- + 3NH_2CSNH_2 + 9H_2O \rightarrow 8Fe(OH)_3 + 3NH_2CONH_2 + 3SO_4^{2-} + 2OH^- \qquad \ldots (1.15)$$

$$8HFeO_4^- + 3CH_3CSNH_2 + 9H_2O \rightarrow 8Fe(OH)_3 + 3CH_3CONH_2 + 3SO_4^{2-} + 2OH^- \qquad \ldots (1.16)$$

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 site (Stevenson and Davies, 1995). 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 *coliforms* 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 3.2x108 /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 ferricand 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 *coliforms*. 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 (Vis_{400}-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.

$$2Fe(VI) + 3As(III) \rightarrow 2Fe(III) + 3As(V) \quad \ldots (1.17)$$

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

Ozernoi, 1995). 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_2FeO_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 8.80×10^{-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_2SO_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 1.0×10^{-4} mol/L to 2.0×10^{-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.

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 it 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 $7.7\times10^{2}M^{-1}\ s^{-1}$ 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), 17*β*-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 parameytric 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 concentartions 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 disruping 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 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 Sarasin, 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 (FeO_4^{2-}/Fe^{3+} and E^0 ($FeO_4^{2-}/Fe(OH)_3$] 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 *viz.*, Mn(VII)/Mn(IV) $E^0 = 1.679$ V and 0.588 V and Cr(VI)/Cr(III) $E^0 = 1.33$ V and -0.12 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 $Fe(OH)_3$, 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 edimentation 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.

CHAPTER

2

METHODOLOGY

2. METHODOLOGY

2.1. Materials and Instrumentations

2.1.1. Chemicals and Apparatus

The chemicals used for the experiments were of AR/GR grade. Bisphenol A ($C_{15}H_{16}O_2$), diclofenac sodium salt ($C_{14}H_{10}C_{12}NNaO_2$), 17α-ethynylestradiol ($C_{20}H_{24}O_2$), 4-tert-octylphenol ($C_{14}H_{22}O$), potassium phthalate monobasic salt ($C_8H_8KO_4$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) were obtained from Sigma Aldrich Co., USA. Diethyl ether ($C_4H_{10}O$), hexane (C_6H_{14}), potassium hydroxide (KOH), hydrochloric acid (HCl), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), disodium hydrogen phosphate (Na_2HPO_4), acetic acid (CH_3COOH) , HPLC Water, acetonitrile HPLC grade (CH_3CN), methanol HPLC grade (CH_3OH) were obtained from Merck India Ltd., India. Moreover, the disodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) was obtained from Himedia, India Ltd., India. Purified sodium hypochlorite (NaClO) was obtained from Palanad Enterprises, Nagpur, India. Purified water (18.2 MΩ cm at 25 °C) was obtained from Millipore Water Purification system (Model: Elix 3). This was fully used for the entire solution preparations and other analytical studies.

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

2.1.2. Reagents

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

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

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

iv. Phosphate buffer: 0.001 mol/L of $Na_2B_4O_7.10H_2O$ and 0.005 mol/L of Na_2HPO_4 were mixed and dissolve in a purified water.

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

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

Lambert’s law which states that ‘the absorbance of the solution containing light absorbing species at a particular wavelength is directly proportional to the concentration of the solution into path length of the sample cell (cm)’.

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

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

2.1.4. Total Organic Carbon Analyser (TOCA)

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

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

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

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

Whether the analysis of TOC is by TC–IC or NPOC methods, it may be broken into three main stages, *viz.,* acidification, oxidation and detection and quantification. The first stage, that is, addition of acid and inert-gas sparging allows all bicarbonate and carbonate ions to be converted in to carbon dioxide, and this IC product vented along with any POC that was present. The release of these gases to the detector for measurement or to the air is dependent upon which type of analysis is of interest, the former for TC–IC and the latter for TOC (NPOC). The second stage is the oxidation of the carbon in the remaining sample in the form of carbon dioxide (CO_2) and other gases. Modern TOC analyzers perform this oxidation step by high temperature oxidation by combustion technique and low-temperature oxidation by employing chemical oxidation (ultraviolet irradiation, heated persulfate, persulfate and UV irradiation combination). Accurate detection and quantification are the most vital components of the TOC analysis process. Conductivity and non-dispersive infrared (NDIR) are the two common detection methods used in modern TOC analyzers. There are some standardized oxidation and detection techniques used in the TOC analyzers and the combination of a specific oxidation and detection method for deriving specific analytical performance range of values is based on some factors like the nature of application or the nature of liquid being tested, and the need which prompted the evaluation.

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

2.1.5. High performance liquid chromatography (HPLC)

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

An HPLC typically includes two columns: an analytical column responsible for the separation and a guard column. The guard column is placed before the analytical column, protecting it from contamination. The most commonly used columns for HPLC are constructed from stainless steel with internal diameters between 2.1 mm and 4.6 mm, and lengths ranging from approximately 30 mm to 300 mm. These columns are packed with 3–10 mm porous silica particles that may have an irregular or spherical shape. Typical column efficiencies are 40,000–60,000 theoretical plates/m. Assuming V_{max}/V_{min} is approximately 50, a 25 cm column with 50,000 plates/m has 12,500 theoretical plates and a peak capacity. In liquid–liquid chromatography the stationary phase is a liquid film coated on a packing material consisting of 3–10 μm porous silica particles. The stationary phase may be partially soluble in the mobile phase, causing it to "bleed" from the column over time. To prevent this loss of stationary phase, it is covalently bound to the silica particles. Bonded stationary phases are attached by reacting the silica particles with an organochlorosilane of the general form $Si(CH_3)_2RCl$, where R is an alkyl or substituted alkyl group.

In reverse-phase chromatography, which is the more commonly encountered form of HPLC, the stationary phase is non polar and the mobile phase is polar. The most common nonpolar stationary phases use an organochlorosilane for which the R group is an *n*-octyl (C_8) or *n*-octyldecyl (C_{18}) hydrocarbon chain. Most reverse phase separations are carried out using a buffered aqueous solution as a polar mobile phase. Because the silica substrate is subject to hydrolysis in basic solutions, the pH of mobile phase must be less than 7.5. The elution order of solutes in HPLC is governed by polarity. In a normal phase separation the least polar solute spends proportionally less time in the polar stationary phase and is the first solute to elute from the column. Retention times are controlled by selecting the mobile phase, with a less polar mobile phase leading to longer retention times. If, for example, a separation is poor because the solutes are eluting too quickly, switching to a less polar mobile phase leads to longer retention times and more opportunity for an acceptable separation. When two solutes are adequately resolved, switching to a more polar mobile phase may provide an acceptable separation with a shorter analysis time. In a reverse phase separation the order of elution is reversed, with the most polar solute being the first to elute. Increasing the polarity of the mobile phase leads to longer retention times, whereas shorter retention times require a mobile phase of lower polarity. When a separation uses a single mobile phase of fixed composition it is called an isocratic elution. It is often difficult, however, to find a single mobile phase composition that is suitable for all solutes. Recalling the general elution problem, a mobile phase that is suitable for early eluting solutes may lead to unacceptably long retention times for later eluting solutes. Optimizing conditions for late eluting solutes, on the other hand, may provide an inadequate separation of early eluting solutes. Changing the composition of mobile phase with time provides a solution to this problem. For a reverse-phase separation the initial mobile-phase composition is relatively polar. As the separation progresses, the mobile phase’s composition is made less polar. Such separations are called gradient elutions. The typical operating pressure of an HPLC is sufficiently high that it is impossible to inject the sample in the same manner as in gas chromatography. Instead, the sample is introduced using a loop injector. Sampling loops are interchangeable and available with volumes ranging from 0.5 mL to 2 mL. In the load position the sampling loop is isolated from the mobile phase and is open to the atmosphere. A syringe with a capacity several times that of the sampling loop is used to place the sample in the loop. Any extra sample beyond that needed to fill the sample loop exits through the waste line. After loading the sample, the injector is turned to the inject position. In this position the mobile phase is directed through the sampling loop, and the sample is swept onto the column. After that the UV detector will detect at a particular wavelength which corresponds to each compounds.

2.2. Analytical methods

2.2.1. Preparation of ferrate(VI)

Ferrate(VI) as potassium ferrate (K_2FeO_4) was prepared adopting the wet chemical oxidation method, with some modifications as described elsewhere (Li *et al.*, 2005; Tiwari *et al.*, 2007). The Fe(III) was oxidized into ferrate(VI) using the sodium hypochlorite (12-14%). The detailed preparation process is described as: 300 mL of chilled NaClO solution was taken in a beaker and 90g of solid KOH was added slowly in this solution and the resulting suspension was again cooled. The precipitate formed was filtered with GF/C filter paper, to give a clear yellow and highly alkaline NaClO solution. The solution was chilled and filtered using a GF/C filter paper to remove any precipitates occurred from the solution. To this solution, 20g of pulverized ferric nitrate was added slowly within *Ca.* 2 hours, with constant and vigorous stirring under cold conditions ($< 8^\circ$ C). Further, after the complete addition of the ferric nitrate, the solution was stirred for another *Ca.* 30 minutes. It was noted that the cold and highly alkaline conditions favored the oxidation of Fe(III) to ferrate(VI). Also the time allowed for stirring may result to achieve an enhanced yield. The color of the solution readily changed yellow brown to purple colour which showed the formation of ferrate(VI). Further, *Ca.* 50g of solid KOH was added slowly; with maintaining the solution temperature $\leq 15^\circ$ C. The solution mixture was allowed to cool standing in a refrigerator for *Ca.* 40 minutes. The resulting dark purple slurry was filtered with a glass filter (medium porosity 10-15µm) and the filtrate was discarded. The precipitate was washed with cold 3M KOH solution (*Ca.* 100 mL (20 mL×5). The filtrate from the washings was collected; taken into a flask and *Ca.* 100 mL of saturated chilled KOH solution was added. The potassium ferrate readily precipitated which was filtered again with a GF/C filter paper. The filtrate was discarded, and the solid was washed with cold 3M KOH solution (*Ca.* 50 mL) and again the filtrate was collected in a beaker. Similarly, re-precipitation was carried out at least for another 3 times to remove any impurities, if present, hence to enhance the purity of ferrate(VI). Finally, the solid was flushed with n-hexane (four times × 10 mL) and diethyl ether (two times × 10 mL). The final product was collected carefully, it was almost black in color and stored in a vacuum desiccator (figure 2.1) along with KOH pellets.

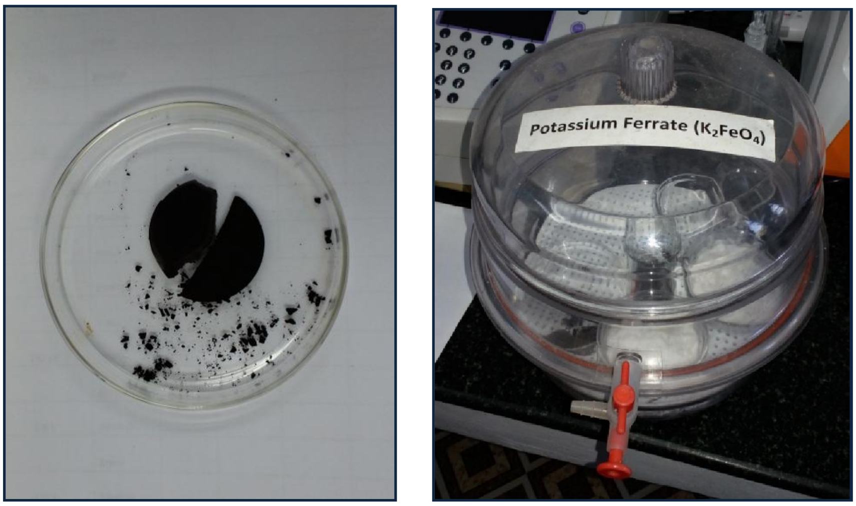


Figure 2.1. Dark purple solid potassium ferrate (K_2FeO_4)

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

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

$$A = \varepsilon . b . C \qquad \dots (2.1)$$

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

ε = molar extinction coefficient of ferrate(VI)

(1150 L/mol/cm at 510 nm at pH 9.2)

b = length of a quartz cell or path length of light (cm)

C = concentration of the soluble ferrate(VI) (mol/L)

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

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

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

The synthesized ferrate(VI) was used to treat different Endocrine disrupting chemicals (EDCs) such as bisphenol A ($C_{15}H_{16}O_2$), diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$), 17α-ethynylestradiol ($C_{20}H_{24}O_2$), 4-tert-octylphenol ($C_{14}H_{22}O$), potassium phthalate monobasic salt ($C_8H_8KO_4$). The degradation of these organic species in the presence of ferrate(VI) was observed indirectly by monitoring the change in the concentration of ferrate(VI) with the help of UV-Visible spectrophotometer.

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

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

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

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

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

2.2.5. Removal of Endocrine disrupting chemicals: HPLC measurements

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

Name of EDCs	**Mobile phase**	**Wavelength (nm)**	**Injection volume (µL)**	**Flow rate (mL/min)**
Bisphenol A (BPA)	Acetonitrile : water (70 : 30)	276	20	0.5
Diclofenac sodium salt (DFS)	Acetonitrile : water : acetic acid (70 : 29 : 1)	276	20	0.5
17α-ethynylestradiol (EE2)	Acetonitrile : water : acetic acid (70 : 29 : 1)	280	20	1
4-tert-octylphenol	Acetonitrile : water (70 : 30)	222	20	1
Potassium phthalate	Acetonitrile : water (70 : 30)	230	20	1

The peak formed at a particular rentention time was corresponded to a particular EDC and it was directly proportional to the concentration of analyte. The peak area was calculated using a software Empower2 and for the estimation of concentration of that EDC. The area of peak calculation was used to obtain the percent removal of EDCs. The results were then presented as percent of EDC removed as a function of EDC concentration and pH. The decrease in pollutant EDCs value of ferrate(VI) treated samples as compared to blank, indicated the extent of degradation of the pollutant under study due to ferrate(VI) treatment.

2.2.6. Effect of background electrolytes and ionic strength

The effect of background electrolytes on the reduction efficiency of ferrate(VI) in presence of different EDCs were investigated using six different types of electrolytes, *viz.,* Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3. A sample solution of EDCs (0.1 mmol/L) was prepared and to it, a known amount of electrolyte was added such that the resulting solution contains molar ratios of EDCs to electrolyte as 1:1. Using drops of dilute HCl/NaOH, the solution was adjusted to pH 8.0. Then, a known amount of ferrate(VI) was added so as to achieve the concentration of ferrate(VI) as 0.1 mmol/L, *i.e.,* the stoichiometric ratios of 1:1:1 for EDCs, electrolyte and ferrate(VI). The change in concentration of ferrate(VI) in the solution was observed recording the absorbance of the solution at the wavelength of 510 nm using UV-Visible spectrophotometer at regular time interval for a specified period. Similarly, absorbance of blank solution, i.e., in absence of EDCs and electrolyte was also recorded for comparison and necessary correction, if needed. The solutions were stirred for 2 hrs and then filtered using the syringe filter (0.45 μm) and divided into two parts and one part was subjected for the measurement of EDCs concentrations using the HPLC and another part was subjected for the total mineralisation of EDcs using the TOC analyser.

In order to further investigate the effect of ionic strength on the degrdation efficiency of EDCs by the ferrate(VI), two electrolytes $NaNO_2$ and Na_2SO_3 were selected. The electrolyte concentrations i.e., 0.01, 0.05, 0.075, 0.1, 0.3 and 0.5 mmol was prepared in the phosphate buffer at pH 8.0 and then the solutions were used for the preparation of EDCs 0.1 mmol/L. Then a known amount of ferrate(VI) was added to achieve the ferrate dose of 0.1 mmol/L was added to the solutions. The change in concentration of ferrate(VI) as a function of time was checked with the help of UV-Visible spectrophotometer (Thermo, UV1). The same experiment was repeated for remaining solutions containing different electrolyte concentrations. The change in total EDCs concentration was checked after filtration of ferrate(VI) treated samples using 0.45 µm syringe filter and was analyzed using an HPLC instrument (Waters, USA; Model : Waters 515 HPLC pump, Waters 2489 UV/Visible detector, C18 5µm (4.6x250 mm column)). Also the mineralisation of EDCs was measured by TOC analyzer (Shimadzu, TOC-$V_{CPH/CPN}$).

CHAPTER

3

RESULTS

AND

DISCUSSIONS

3. RESULTS AND DISCUSSION

Degradation of organic species by ferrate(VI) : Batch reactor analysis

3.1. Bisphenol A (BPA)

3.1.1. Degradation of bisphenol A (BPA) using UV-Vis measurements

3.1.1.1. Effect of concentration of BPA

Bisphenol A was treated at different pH (i.e., pH 7.0 to 12.0) conditions and at varied molar ratios of ferrate(VI) to BPA (i.e., from 1:0.3 to 1:5). In other words, the BPA concentration was varied from 0.03 mmol/L to 0.5 mmol/L with a constant ferrate(VI) dose of 0.1 mmol/L. The results are presented graphically in figure 3.1 for the BPA (at pH 8.0 is taken as representative graph). A similar degradation pattern was obtained at other pH values as well. In general, it was reported previously that the aqueous decomposition of ferrate was depended strongly on the initial ferrate concentration, co-existing ions, pH, and temperature (Jiang and Lloyd, 2002). It is evident from the figure that increasing the concentration of BPA the reduction of ferrate(VI) is increased sharply. Therefore, the degradation of the pollutants are increased significantly with the increase of pollutant concentration at a constant dose of ferrate(VI). Further, it is observed that the ferrate(VI) concentration is decreased sharply during the initial period of contact followed by an apparent equilibrium or the constant concentration of ferrate(VI) is obtained. The maximum decrease of ferrate(VI) concentration was observed within initial *Ca* 5 minutes of contact in presence of BPA. This showed that the ferrate(VI) is found to be quite efficient in the degradation of pollutant from aqueous solutions. Quantitatively, increasing the contact time from 0 to 20 min the amount of ferrate(VI) was decreased from 0.10 to 0.013 mmol/L for BPA in the 1:1 molar ratio of ferrate(VI) to BPA concentration. It was noted that relatively the degradation of BPA was high using the ferrate(VI) dose of 0.1 mmol/L at varied concentrations of BPA. BPA molecule was contained with two dissociable hydrogen atoms. The values of pk_a^1 and pk_a^2 were reported to be 9.9 and 10.2, respectively (Tian *et al.*, 2009). It was assumed that ferrate(VI) could quickly cause to open the bond of two phenyl groups present with BPA molecule and therefore, showed gradual oxidation of BPA (Zhang *et al.*, 2012). Moreover, it was reported previously that the oxidation of phenol were proceeded with the 1e$^-$ and 2e$^-$ process by the ferrate(VI). The formation of phenoxy radicals, Fe(V) followed with the diphenols and p-benzoquinone was identified in such oxidation process (Huang *et al.*, 2005)

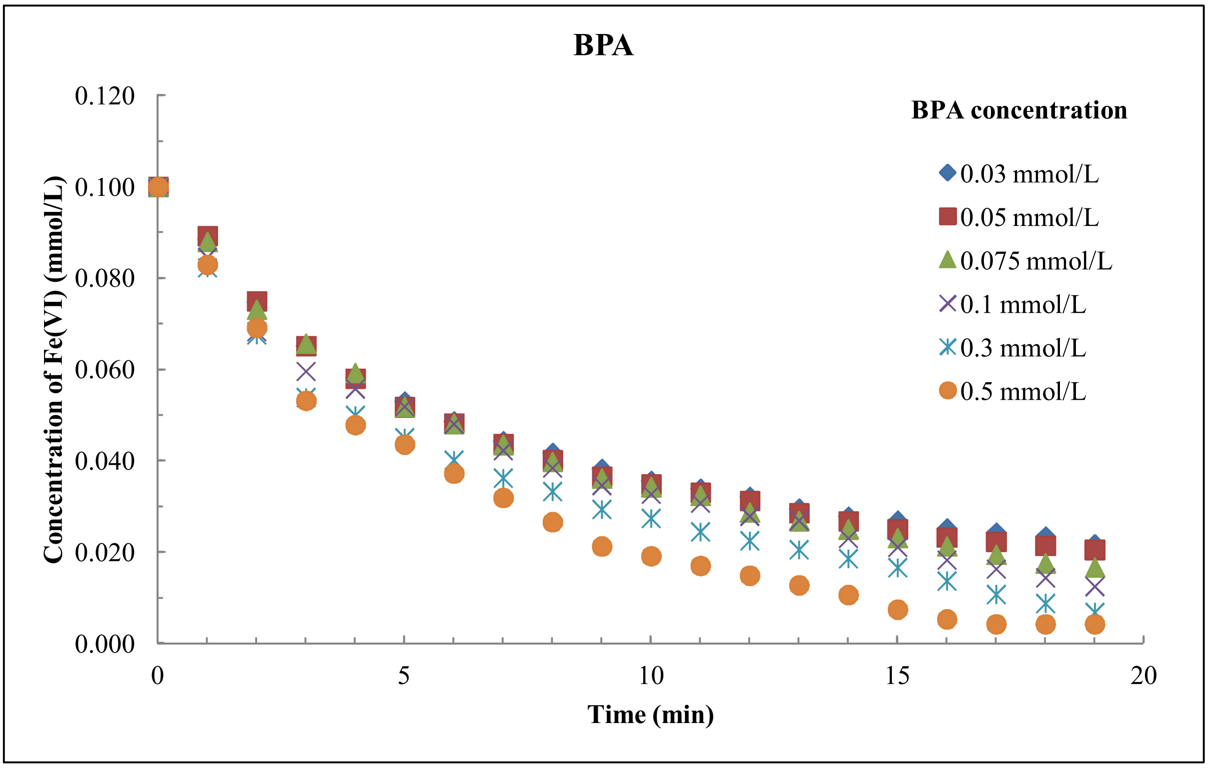


Figure 3.1 Degradation of BPA as a function of time for different concentration of BPA for the constant ferrate(VI) dose of 0.1 mmol/L ferrate(VI) at constant pH 8.0.

3.1.1.2.Kinetics of ferrate(VI) degradation

The degradation kinetic is an useful parameter to be estimated to correlate the efficiency of ferrate(VI) in the degradation of pollutants. Therefore, the kinetics of BPA degradation by ferrate(VI) was obtained at neutral pH 7.0. The rate expression of ferrate(VI) reduction in presence of BPA could be written as in equation (3.1):

$$-\frac{d[Fe(VI)]}{dt} = k_{app}\ [Fe(VI)]^m\ [BPA]^n \qquad \ldots(3.1)$$

where k_{app} is the apparent rate constant of the degradation of ferrate(VI) in presence of BPA. Further, at varied concentration of the BPA, the above equation could be reduced to equation (3.2):

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)]^m \qquad \ldots(3.2)$$

where, $k = k_{app}\ [BPA]^n$ …(3.3)

Using the time dependence change in ferrate(VI) concentration observed at UV_{510}, the data was utilized to fit into the pseudo-first-order rate and pseudo-second-order rate equations as to optimize the value of ‘m’ to 1 or 2. It was observed that the kinetic data is reasonably fitted well to the pseudo-second order rate kinetics and indicated that the value of ‘m’ is 2 with respect to the degradation of ferrate(VI) in presence of BPA. Therefore, the pseudo-second order rate constant values were estimated and returned in table 3.1 with the regression coefficient (R^2). It is clearly observed that increasing the BPA concentration (from 0.03 to 0.5 mmol/L) was caused significantly to increase the pseudo-second order rate constant values for the BPA. This was due to the fairly high oxidizing capacity of ferrate(VI) towards the pollutants which enables it degrade pollutants readily from aqueous solutions (García- Araya *et al.*, 2010).

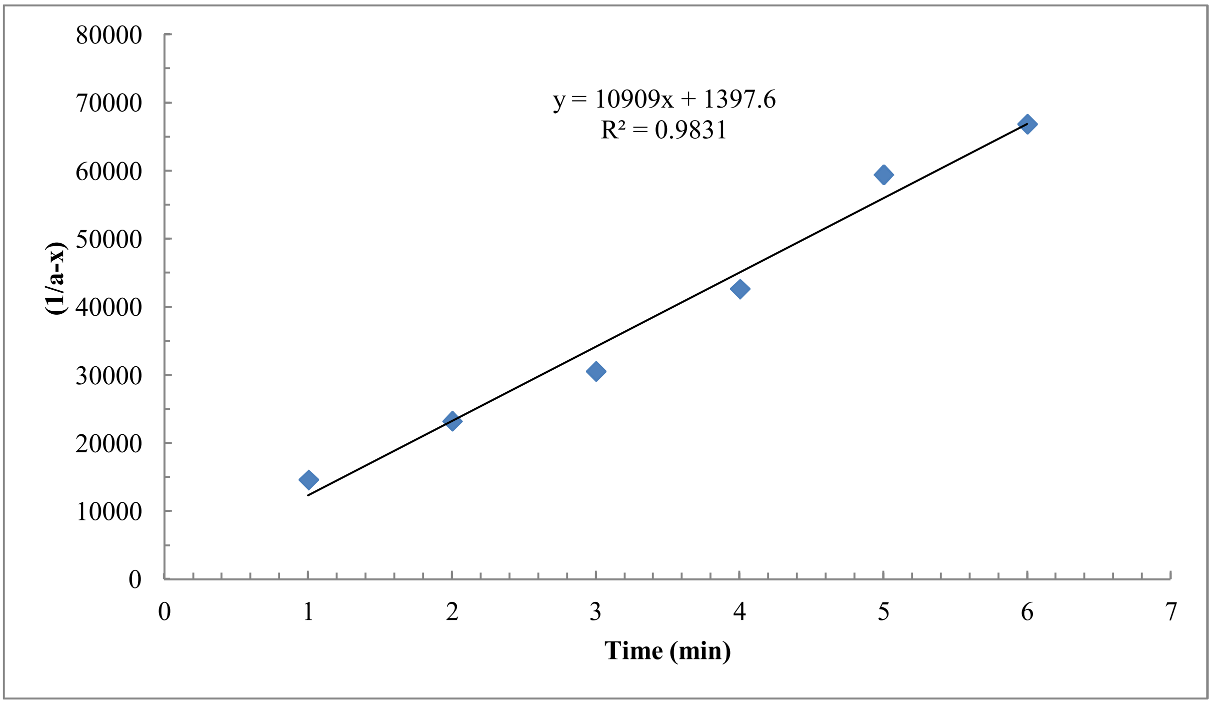


Figure 3.*2* Pseudo second order rate kinetics for ferrate(VI) in presence of BPA at pH 7.0 (Concentration of ferrate(VI) : 0.1 mmol/L, Concentration of BPA : 0.1 mmol/L)

Table 3.1 Pseudo-second order rate constants estimated in the degradation of ferrate(VI) in presence of BPA at pH 7.0.

Ferrate(VI) concentration (mmol/L)	**BPA concentration (mmol/L)**	**Pseudo-second order rate constant k (L/mol/min)**	**R^2**
0.1	0.03	1085.6	0.983
0.1	0.05	4597.0	0.972
0.1	0.075	5312.0	0.997
0.1	0.1	10909.0	0.983
0.1	0.3	12155.0	0.981
0.1	0.5	27721.0	0.964

Further, the value of 'n' along with the apparent rate constant value k_{app} was estimated using the pseudo-second order rate constant values obtained at varied concentrations of BPA at pH 7.0. The plots were drawn between the concentrations of BPA against the estimated k values and returned in figure 3.3. It was clearly demonstrated that the data was reasonably fitted well and hence the value of n was found to be 1. Therefore, the stoichiometric ratio of the ferrate(VI) with BPA was found to be 2:1. Moreover, the overall rate constant k_{app} was estimated to be 53642.0 L/mol/min at pH 7.0. Previously, it was reported the degradation of E2, EE2 and bisphenol A was followed the second order rate law and the rate constant values were ranged from the 6.4×10^2 to 7.7×10^2 L/mol/s at pH 7.0 (Lee *et al.*, 2005).

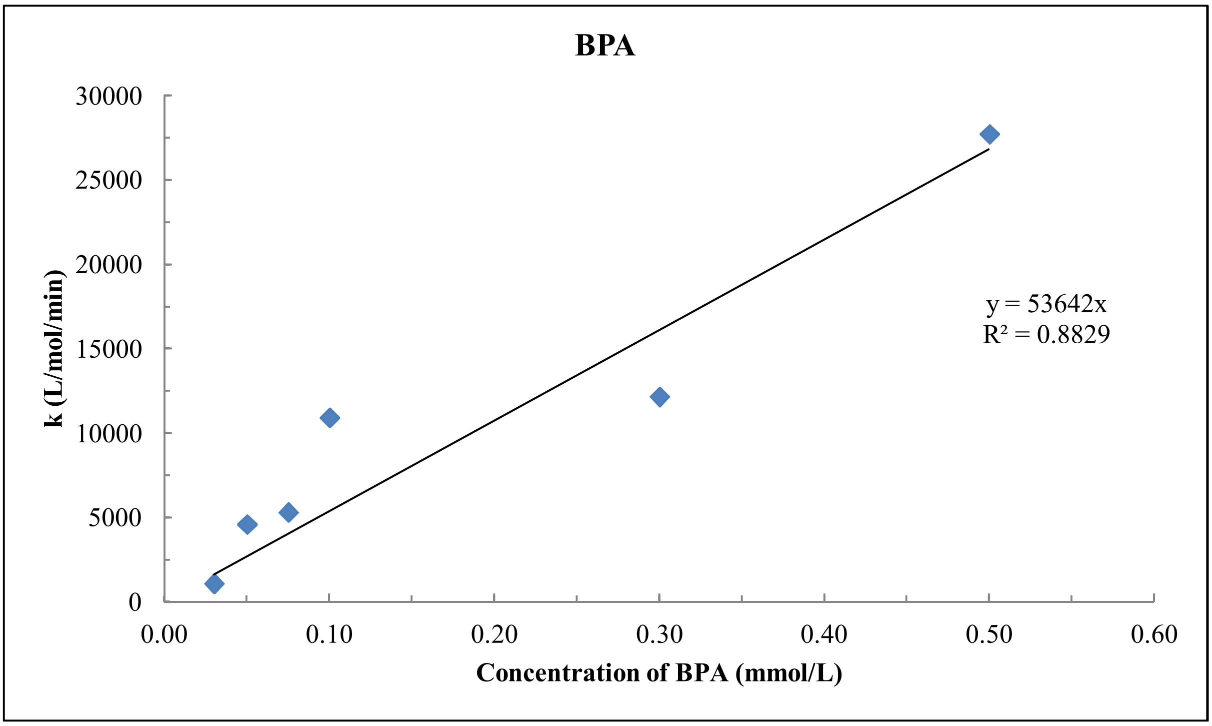


Figure 3.3 Variation of pseudo-second order rate constants (k) values as a function of BPA at pH 7.0.

3.1.2. Oxidative removal of BPA using HPLC measurements

The ferrate(VI) BPA samples are filtered with the 0.45 µm syringe filter and the filtrates were subjected for the BPA concentration measurements using pre-calibrated high performance liquid chromatography (HPLC). The mobile phase was employed as acetonitrile : water (70:30, v/v) with a flow rate of 0.5 mL/min. An injection volume of 20 µL was used and the concentration of BPA was determined at 276 nm. The HPLC chromatograms for blank BPA and ferrate(VI) treated BPA sample were represented in figure 3.5 (a representative sample 1:1 BPA to ferrate(VI) treated at pH 7.0). It was observed that the retention time occurred for BPA was 7.1 minute. Further, the HPLC chromatogram, i.e. peak area was calculated using the EMPOWER2 Software in µV*sec unit which corresponds to the concentration of BPA in an aqueous solution. The concentration of BPA was varied from 0.03 mmol/L to 0.5 mmol/L whereas the concentration of ferrate(VI) was kept constant at 0.1 mmol/L. In other words, the ferrate(VI) : BPA molar ratios were 1:0.3, 1:0.5, 1:0.75, 1:1, 1:3 and 1:5. Moreover, all these different molar concentrations samples were treated at varied pH values i.e., pH 7.0 to 12.0. The ferrate(VI) treated BPA peak area was compared with the blank BPA peak area and the hence, the percent BPA removal was calculated. The results are returned in table 3.2 and graphically in figure 3.4. It was found that 99.23% of BPA was removed at 0.1 mmol/L of ferrate(VI) and 0.03 mmol/L of BPA at pH 7.0 as shown in the table 3.4. The percent removal of BPA was decreased as the concentration of BPA was increased at constant dose of ferrate(VI). On the other hand, the percent removal of BPA was decreased with the increase in pH i.e., from pH 7.0 to 12.0 for all these studied molar ratios. Therefore, relatively, a high percent removal of BPA was obtained at pH 7.0. This is due to the fact that the reduction potential of ferrate(VI) was gradually increased with lowering the solution pH. This indicated that the reactivity of ferrate(VI) was increased significantly decreasing the pH (Jiang, 2007; Lee *et al.*, 2004). Similarly, the percent removal of BPA was decreased as the pH of the aqueous solution was increased from pH 7.0 to 12.0. At pH 7.0, in the ferrate(VI) : BPA molar concentration 1:1, the percent removal was 88.60% and the overlay peaks of BPA (red) and BPA treated with ferrate(VI) (green) was shown in the figure 3.5. It was also noted that the ferrate(VI) treated BPA chromatogram were possessed with some additional peaks. This possibly represented that some stable degraded by-products were formed.

Table 3.2 Percent Removal of BPA species by ferrate(VI) at different pH and molar ratio values.

pH	Initial concentration (mmol/L)		Area (µV*sec)	% Removal
	Ferrate(VI)	Bisphenol A		
7.0	0	0.03	121757	99.23
	0.1	0.03	936	
	0	0.05	215480	99.03
	0.1	0.05	2099	
	0	0.075	327287	98.10
	0.1	0.075	6217	
	0	0.1	382985	88.60
	0.1	0.1	43677	
	0	0.3	1091847	65.05
	0.1	0.3	381583	
	0	0.5	1818637	52.35
	0.1	0.5	866491	
8.0	0	0.03	294535	94.00
	0.1	0.03	17672	
	0	0.05	562565	87.96
	0.1	0.05	67755	
	0	0.075	847042	73.89
	0.1	0.075	221187	
	0	0.1	1152680	59.94
	0.1	0.1	461793	
	0	0.3	3144743	52.54
	0.1	0.3	1492387	
	0	0.5	5200485	35.00
	0.1	0.5	3380315	
9.0	0	0.03	452665	92.66
	0.1	0.03	33225	
	0	0.05	616547	82.98
	0.1	0.05	104947	
	0	0.075	890776	74.27
	0.1	0.075	229178	
	0	0.1	1180570	70.83
	0.1	0.1	344348	
	0	0.3	3393467	46.91
	0.1	0.3	1801728	
	0	0.5	5295275	30.38
	0.1	0.5	3686700	

pH	**Initial concentration (mmol/L)**		**Area (μV*sec)**	**% Removal**
	Ferrate(VI)	**Bisphenol A**		
10.0	0	0.03	342487	79.17
	0.1	0.03	71324	
	0	0.05	536326	73.22
	0.1	0.05	143650	
	0	0.075	741959	61.86
	0.1	0.075	282961	
	0	0.1	812552	60.02
	0.1	0.1	324854	
	0	0.3	2988648	54.16
	0.1	0.3	1369950	
	0	0.5	3936880	16.03
	0.1	0.5	3305784	
11.0	0	0.03	321241	73.95
	0.1	0.03	83681	
	0	0.05	428346	54.36
	0.1	0.05	195508	
	0	0.075	627474	47.67
	0.1	0.075	328377	
	0	0.1	850688	43.39
	0.1	0.1	481612	
	0	0.3	2491945	34.40
	0.1	0.3	1634693	
	0	0.5	3979470	17.34
	0.1	0.5	3289238	
12.0	0	0.03	248626	35.00
	0.1	0.03	161606	
	0	0.05	411888	27.00
	0.1	0.05	300678	
	0	0.075	623103	23.80
	0.1	0.075	474784	
	0	0.1	853412	22.95
	0.1	0.1	657584	
	0	0.3	2386479	12.45
	0.1	0.3	2089406	
	0	0.5	3989677	4.89
	0.1	0.5	3794607	

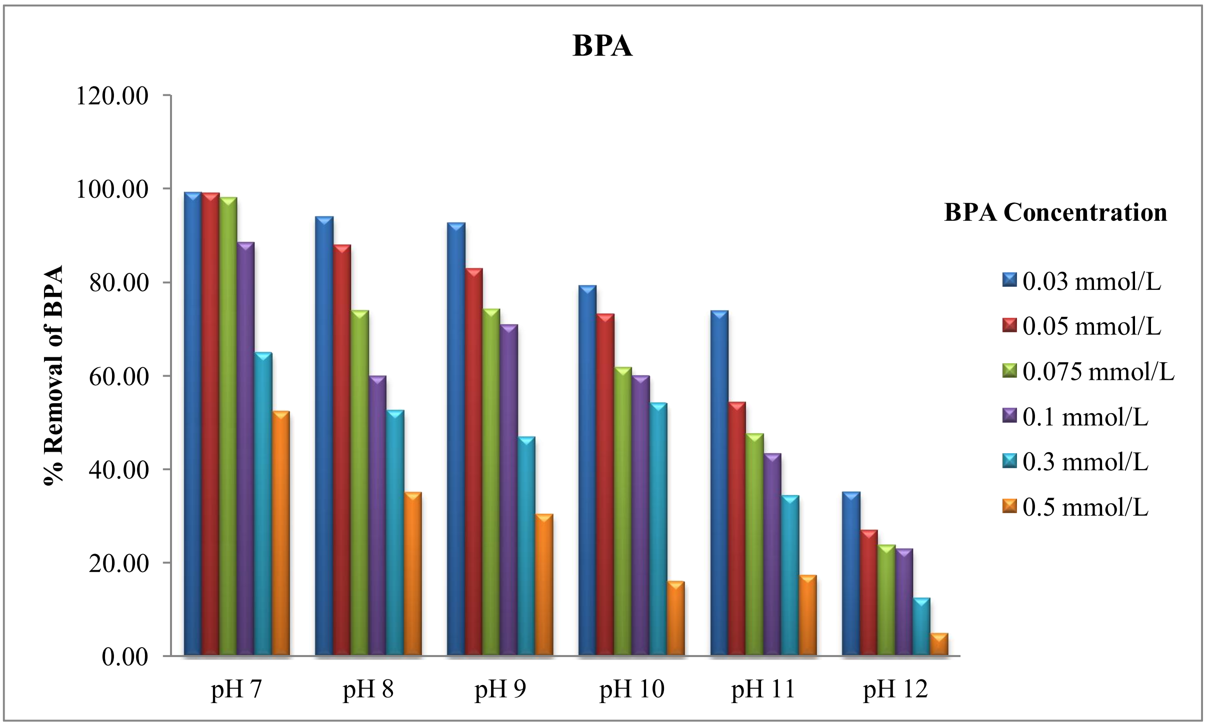


Figure 3.4 Percent removal of BPA as a function of solution pH and BPA concentrations using a constant dose of Fe(VI) : 0.1 mmol/L.

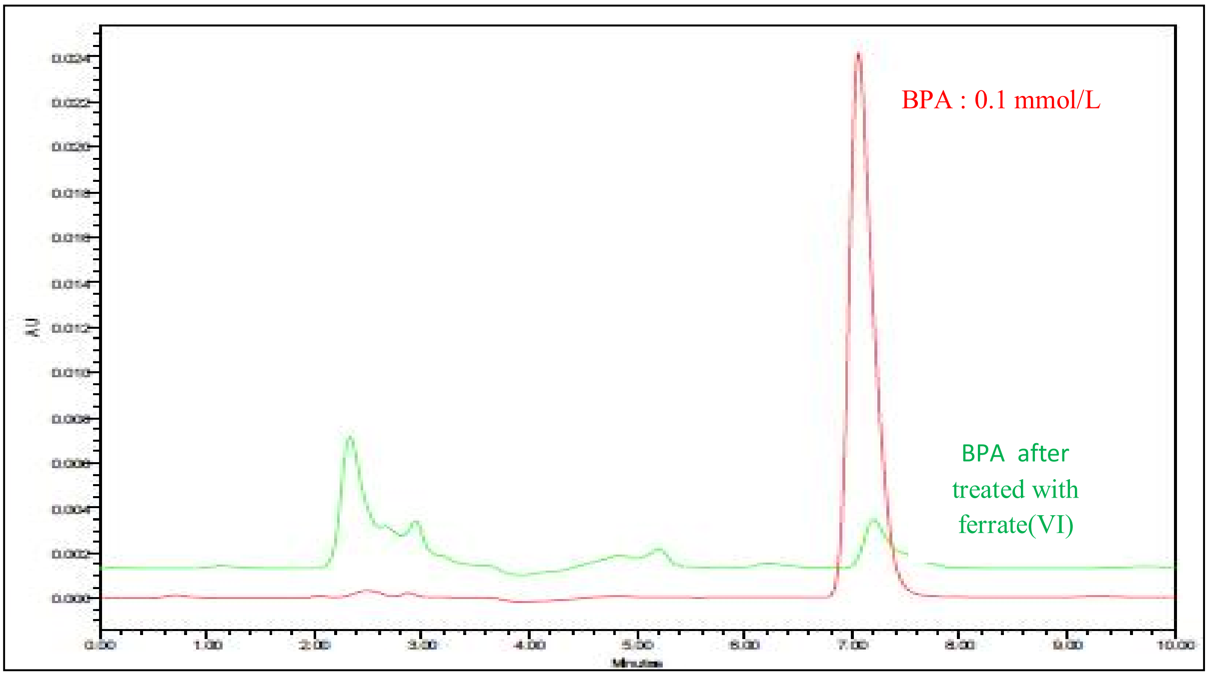


Figure 3.5 Degradation of BPA at Fe(VI) : BPA molar ratio 1:1 (pH 7.0).

3.1.3. Effect of pH in the degradation of BPA with ferrate(VI)

The pH dependence degradation of BPA by ferrate(VI) is an useful parameter in order to optimize the selectivity of solution pH to degrade the BPA from aqueous solution. Additionally, it provides a plausible mechanism that involved in the degradation of BPA with ferrate(VI). The degradation of BPA as studied previously as a function of pH was presented in figure 3.4 as percent removal of BPA against the solution pH and concentration of micro-pollutants. It was observed, in general, that increasing the concentration of BPA caused to decrease in percent removal of BPA at a constant dose of ferrate(VI). More quantitatively, increasing the concentration of BPA from 0.03 to 0.5 mmol/L the corresponding decrease in percent removal of BPA was found to be from 99.23 to 52.35%, respectively at pH 7.0 and at ferrate(VI) dose of 0.1 mmol/L. This decrease in percent removal was due to the fact that at lower concentration of BPA relatively more number of ferrate(VI) molecules were present to degrade the lesser number of BPA molecules. However, increasing the concentration of BPA an apparent increase in content of BPA removal was obtained. This indicated that although at lower concentration the percent removal of BPA was higher however, the increase in pollutant concentration was favoured the content removal of pollutant at constant dose of ferrate(VI).

On the other hand the decrease in pH from pH 12.0 to 7.0 enabled to increase significantly the percent removal of BPA from aqueous solutions (*cf* figure 3.4). Quantitatively, decreasing the pH from 12.0 to 7.0 the corresponding percent degradation of BPA was increased from 22.95 to 88.60% at the ferrate(VI) to BPA molar ratio 1:1. The speciation studies conducted elsewhere showed that at around pH 7.0 the protonated species of the ferrate(VI) i.e., $HFeO_4^-$was dominated since the pK_a value for the acid dissociation of $HFeO_4^-$ was reported to be 7.3 (Sharma *et al*., 2001):

$$HFeO_4^- \leftrightarrow FeO_4^{2-} \qquad (pk_a=7.3) \qquad \ldots(3.4)$$

The reactivity of protonated species was significantly increased due to the protonated species were possessed with greater spin density (Ohta *et al.*, 2001; Sharma *et al.*, 2004). Moreover, the alkyl groups were found to be electron releasing groups, hence enhanced the reactivity of protonated species $HFeO_4^-$ in aqueous solutions (Sharma, 2013). Similarly, the redox potential of ferrate(VI) was gradually increased with the decrease in pH which again enhanced the reactivity of the ferrate(VI) at lower pH conditions. Previously, it was reported that 4-chlorophenol was degraded maximum at pH 9.0 whereas relatively less degradation was achieved at pH 11 and 7.0. This was explained with the fact that at this pH phenol was predominantly present in the deprotonated species which was readily attacked by the ferrate(VI) and led to the formation of phenoxy radicals (Graham *et al.*, 2004). Similarly, the higher degradation was reported with the protonated species of ferrate ($HFeO_4^-$) than the deprotonated species (FeO_4^{2-}) in the degradation of various steroid estrogen including BPA from aqueous solutions (Li *et al.*, 2008).

It was further noted that at 1:0.3 molar ratio of Fe(VI) : BPA at pH 7.0 the BPA was removed completely. In a line, previously it was reported that the dissociated species of ciprofloxacin was relatively stable whereas the un-dissociated species of ciprofloxacin was unstable. Therefore, the degradation of dissociated species by ferrate(VI) was found lesser than the un-dissociated ciprofloxacin (Jiang *et al.*, 2012). Additionally, the electron releasing alkyl groups possessed by the BPA molecule was further enhanced its degradation by ferrate(VI) (Sharma, 2013)

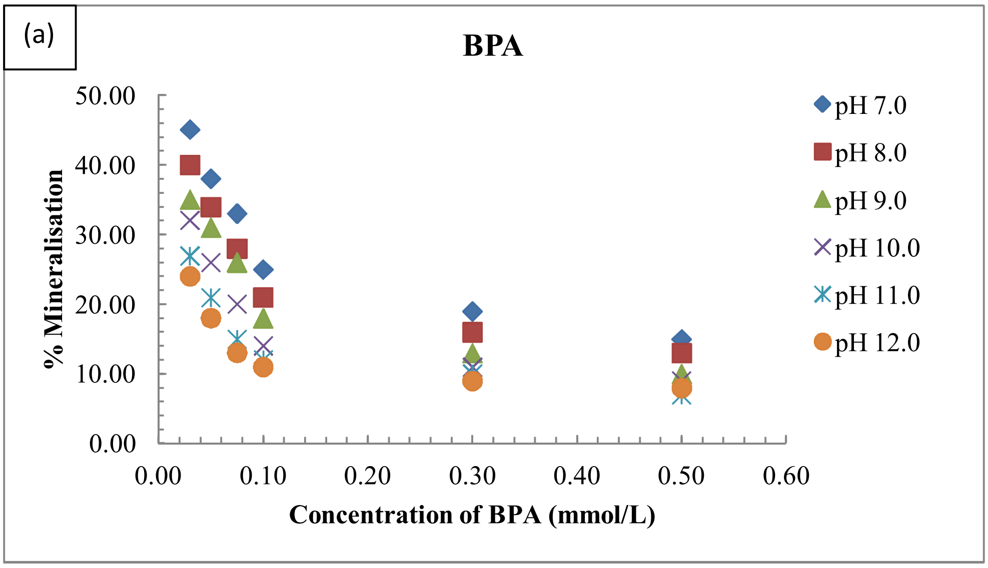
3.1.4. Mineralization of BPA

Further, it is interesting to obtain the mineralization of the BPA with the ferrate(VI) treatment. The samples of BPA having varied concentrations (0.03 to 0.5 mmol/L) were treated with a constant dose of ferrate(VI) for a period of 2 hrs at constant but varied pH conditions (pH 7.0 to 12.0) and then the samples were subjected for the estimation of the total TOC (total organic carbon) values. The untreated samples of BPA (i.e., blank samples) were also used to measure the initial TOC values. Based on the TOC measurements, the percent TOC removal of the BPA was obtained and presented as a function of BPA concentrations and solution pH vide figure 3.6(a) and Table 3.3. It is evident from the figure 3.6(a) or Table 3.3 that the decrease in BPA concentration and pH was greatly favoured the percent removal of TOC. Quantitatively, decreasing the BPA concentration from 0.5 to 0.03 mmol/L was caused to increase the TOC removal from 15.01 to 45.12% as observed at pH 7.0. Similarly, decreasing the solution pH from 12.0 to 7.0 the corresponded increase in percent TOC removal was found to be 11.03 to 25.03% at the 1:1 molar ratio of the ferrate(VI) to BPA. The trend of this result is quite in a line to the kinetic and HPLC results obtained previously. It was also evident from the TOC data that although a partial mineralization of BPA was obtained but a significant percent was mineralized with the single dose of ferrate(VI).

On the other hand the data is further presented in terms of total amount of the BPA mineralized by the ferrate(VI) treatment and were presented as function of BPA initial concentration and solution pH (*cf* figure 3.6(b)) . It was interesting to observe that increasing the concentration of BPA was favoured significantly the content of BPA removal from aqueous solutions. Whereas the decrease in pH (i.e., from pH 12.0 to 7.0) favoured the content removal of BPA.

Table 3.3 Percent mineralisation of BPA by ferrate(VI) at different pH and BPA concentrations (Fe(VI) concentration 0.1 mmol/L)

pH	**% Mineralisation of BPA by ferrate(VI)**					
	[Fe(VI)] : [Bisphenol A]					
	1:0.3	**1:0.5**	**1:0.75**	**1:1**	**1:3**	**1:5**
7.0	45.12	38.06	33.05	25.03	19.00	15.01
8.0	40.04	33.98	28.02	21.01	16.01	13.01
9.0	35.06	31.04	26.04	18.02	13.01	10.01
10.0	32.09	26.04	20.07	14.05	11.00	9.01
11.0	26.98	20.98	15.00	12.04	10.01	7.01
12.0	24.04	18.05	13.07	11.03	9.01	8.01



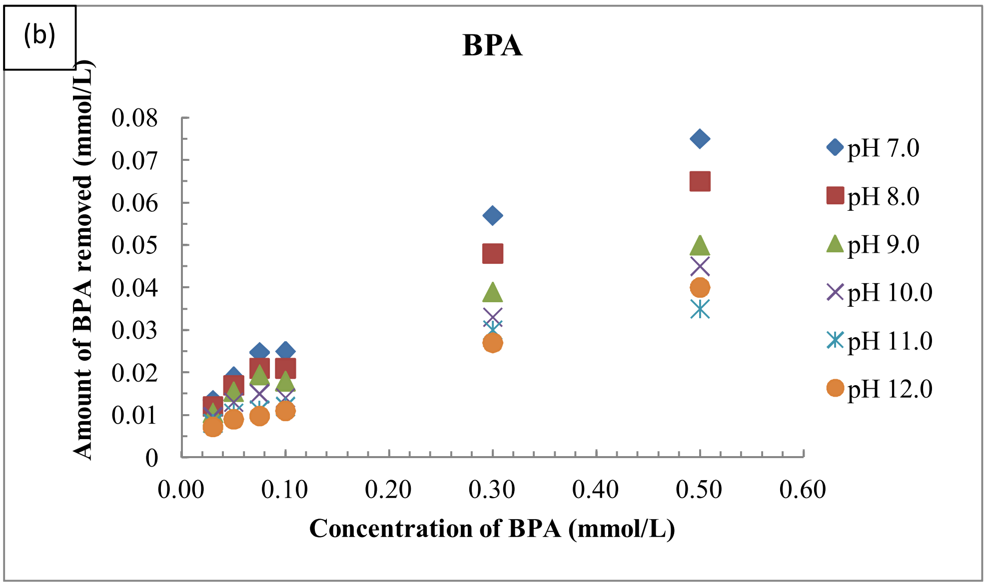


Figure 3.6 (a) Percent mineralisation; and (b) extent removal of BPA as a function of pH and BPA concentrations at a constant dose of ferrate(VI) : 0.1 mmol/L.

3.1.5. Effect of background electrolytes

The presence of co-exiting ions in the oxidative removal of BPA (0.1 mmol/L) was studied using the ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3 were used as co-existing ions. Variety of electrolytes was used having partly or fully oxidized ions. The results were returned in graphically in figure 3.7 for BPA. Results indicated that the presence of fully oxidized electrolytes viz., NaCl, $NaNO_3$ and Na_2HPO_4 were not affected significantly the oxidation of BPA by ferrate(VI). The presence of phosphate and nitrate caused to increase slightly the degradation of the BPA. This was due to the fact that ferrate(VI) was relatively stable in the phosphate media forming complexes with Fe(III) otherwise forming precipitates of iron oxide and which accelerated the spontaneous fast decomposition of ferrate(VI) (Thompson *et al.*, 1951). However, on the other hand the partly oxidized $NaNO_2$ and Na_2SO_3 species were caused significantly to decrease the decomposition of BPA from aqueous solutions. The results inferred that the presence of NO_2^- and SO_3^{2-} were affected the degradation of BPA up to some extent by the ferrate(VI). Previously, it was reported that the presence of NO_2^- and SO_3^- greatly affected the degradation of the Zn(II)-NTA complex species by the ferrate(VI) since the ferrate(VI) decomposition was increased significantly in presence of these electrolytes (Yang *et al.*, 2010). Further, the extent of oxidation of BPA by the ferrate(VI) was studied increasing the $NaNO_2$ or Na_2SO_3 concentration from 0.1 to 5.0 mmol/L at the constant BPA and ferrate(VI) concentration of 0.1 mmol/L and at pH 8.0. These results were returned graphically in figure 3.8. It was noted that increasing the background concentration from 0.1 to 5.0 mmol/L $NaNO_2$ the corresponding decrease in percent removal of BPA was from 55.54 to 50.42 % (i.e., 5.12% only), respectively. Similarly, increasing the Na_2SO_3 concentration from 0.1 to 5.0 mmol/L, the corresponding decrease in percent removal of BPA was decreased from 53.61 to 47.56 % (i.e., 6.05% only), respectively. The insignificant decrease in percent removal of BPA even with increasing the partly oxidized electrolytes *viz.*, $NaNO_2$

and Na_2SO_3 pointed the affinity and potential application of ferrate(VI), at least, in the degradation of BPA from aqueous solutions.

Similar, to HPLC data the TOC data was also obtained in order to estimate the percent mineralization of BPA by ferrate(VI) in presence of various background electrolytes at pH 8.0 and ferrate(VI) to BPA molar ratio 1:1. The results were returned graphically in figure 3.9 and in Table 3.5. A partial mineralization was not significantly affected in presence of studied electrolytes. Similarly, the presence of partially oxidized electrolytes viz., $NaNO_2$ and Na_2SO_3 also was not affected significantly the mineralization of BPA by ferrate(VI) vide Figure 3.10. This result was in a line to the HPLC data obtained previously.

Table 3.4 Percent removal of BPA by ferrate(VI) as a function of different background electrolytes at pH 8.0. (HPLC measurement) (Blank=59.94% removed)

Electrolyte	**Area (µV*sec)**		**% Removal**
	BPA	**BPA + Electrolyte + Ferrate(VI)**	
Na_2HPO_4	1152680	457383	60.32
Na_2SO_4	1152680	464875	59.67
$NaNO_3$	1152680	447124	61.21
NaCl	1152680	462801	59.85
$NaNO_2$	1152680	512481	55.54
Na_2SO_3	1152680	534728	53.61

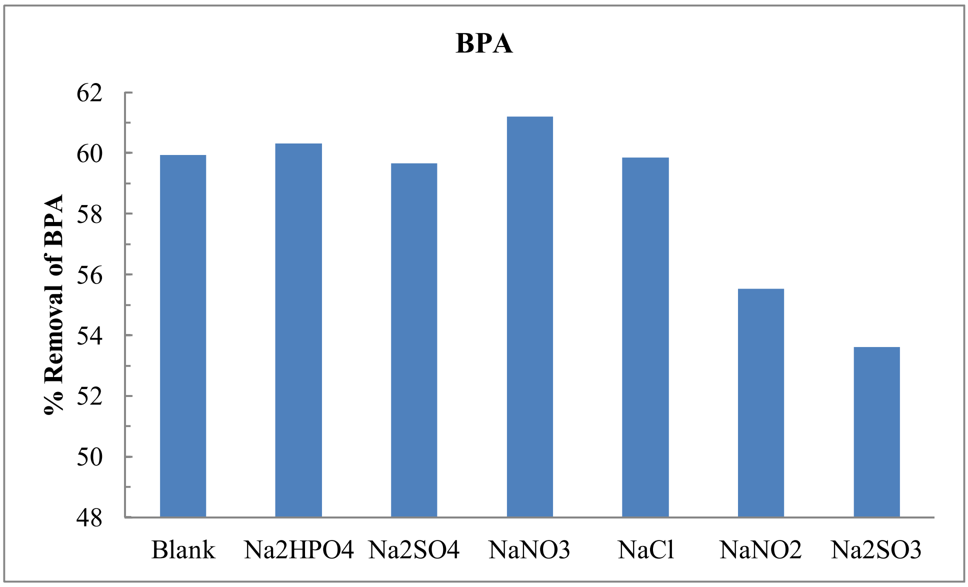


Figure 3.7 Effect of electrolytes in the degradation of BPA by ferrate(VI) at pH 8.0.

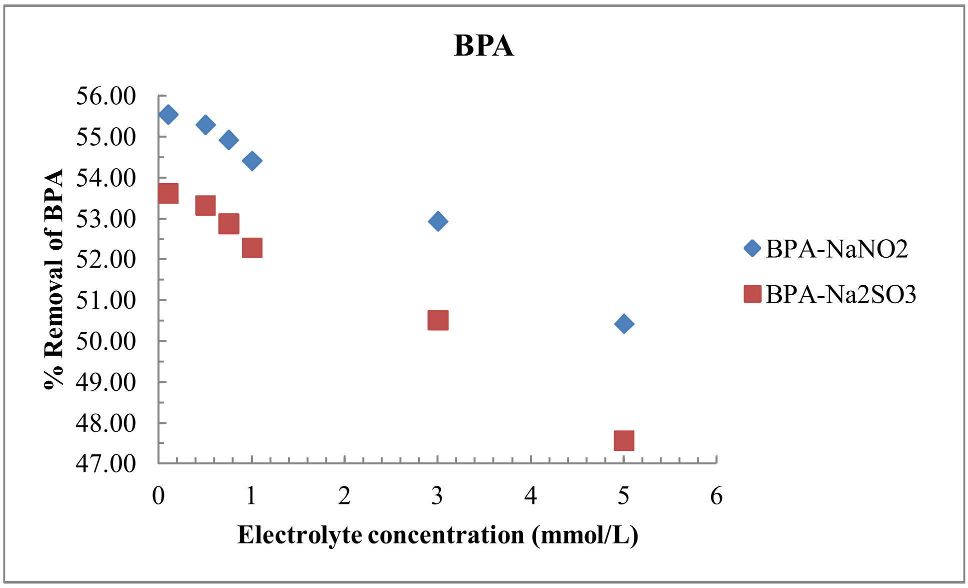


Figure 3.8 Effect of various concentrations of electrolyte in the degradations of BPA by ferrate(VI).

Table 3.5 Percent mineralisation of BPA by ferrate(VI) as a function of different background electrolytes at pH 8.0. (TOC measurement) (Blank=21% mineralization)

Electrolyte	**Total Organic Carbon (mg/L)**		**% Mineralisation**
	BPA	**BPA + Electrolyte + Ferrate(VI)**	
Na_2HPO_4	18.28	14.22	22.21
Na_2SO_4	18.28	14.36	21.44
$NaNO_3$	18.28	14.39	21.28
NaCl	18.28	14.24	22.10
$NaNO_2$	18.28	14.68	19.69
Na_2SO_3	18.28	14.92	18.38

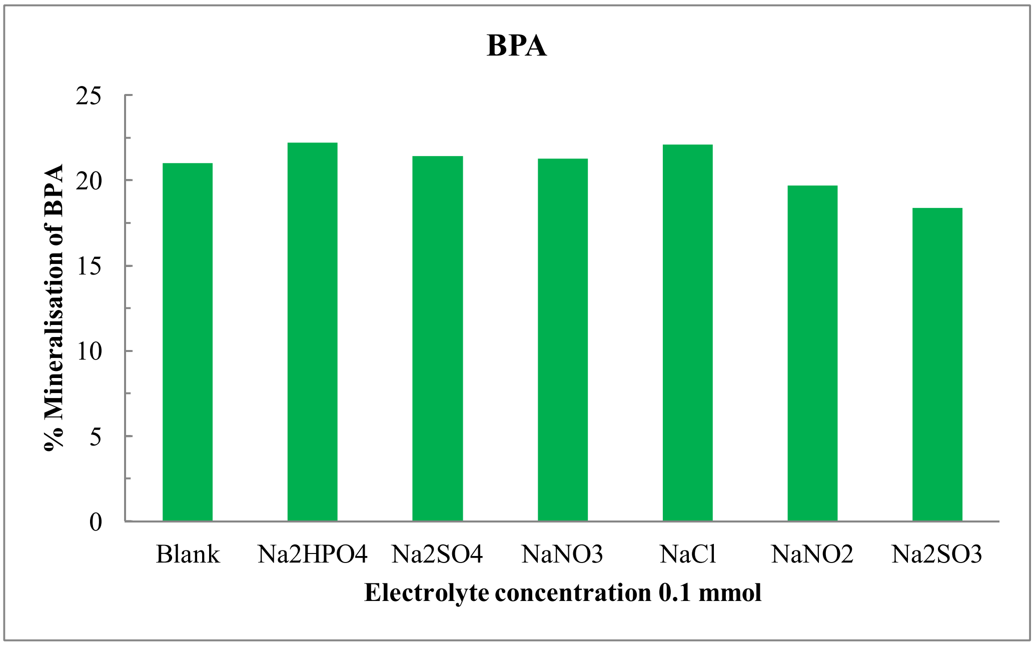


Figure 3.9 Effect of electrolytes in the mineralization of BPA by ferrate(VI) at pH 8.0.

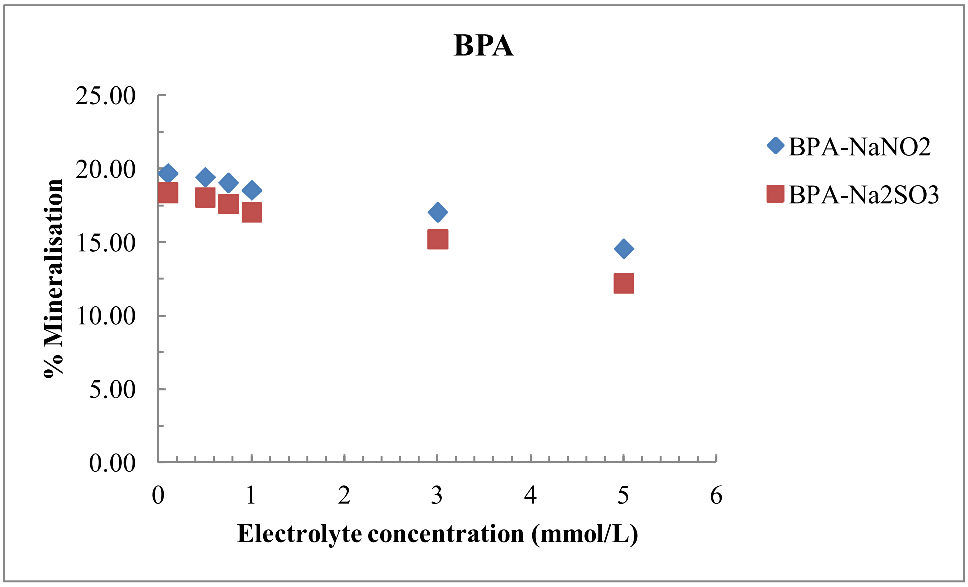


Figure 3.10 Effect of various concentrations of electrolytes $NaNO_2$ and Na_2SO_3 in the mineralization of BPA by ferrate(VI).

3.2. Diclofenac sodium (DCF)

3.2.1. Degradation of diclofenac sodium using UV-Vis measurements

3.2.1.1. Effect of concentration of diclofenac sodium

The diclofenac sodium was treated with ferrate(VI) at different pH (i.e., pH 7.0 to 12.0) conditions and at varied molar ratios of ferrate(VI) to diclofenac (i.e., from 1:0.3 to 1:5). In other words, the diclofenac concentration was varied from 0.03 mmol/L to 0.5 mmol/L at a constant ferrate(VI) dose of 0.1 mmol/L. The results are presented graphically in figure 3.11 for the diclofenac (at pH 8.0 is taken as representative graph). It is evident from the figure that increasing the concentration of diclofenac the reduction of ferrate(VI) was increased sharply. Therefore, the degradation of the pollutants were increased significantly with the increase of pollutant concentration at a constant dose of ferrate(VI). Further, it was observed that the ferrate(VI) concentration was decreased sharply during the initial period of contact followed by an apparent equilibrium or the constant concentration of ferrate(VI) was obtained. The maximum decrease of ferrate(VI) concentration was observed within an initial *Ca* 5 minutes of contact in presence of this pollutant. This showed the greater efficiency of ferrate(VI) in the degradation of pollutants from aqueous solutions. Quantitatively, increasing the contact time from 0 to 20 min the amount of ferrate(VI) was decreased from 0.10 to 0.053 mmol/L for diclofenac in the 1:1 molar ratio of ferrate(VI) and diclofenac. It was also noted that the degradation of diclofenac was relatively high using the ferrate(VI) dose of 0.1 mmol/L at varied concentrations of diclofenac sodium. The degradation rate of DCF was relatively slower than the BPA degradation. Diclofenac which possessed low dipole moment and acid dissociation constant value was found to be pK_a: 4.21 (Meloun et at., 2007). Therefore, the DCF was predominantly present in the solution as deprotonated form within the studied pH region i.e., pH 7.0 to 12.0. It was previously reported that the diclofenac sodium molecule possess a nucleophilic center (amino group) where it readily interacted with an electrophilic agent as ozone and caused to initiate the degradation of DCF molecule (García- Araya *et al.*, 2010).

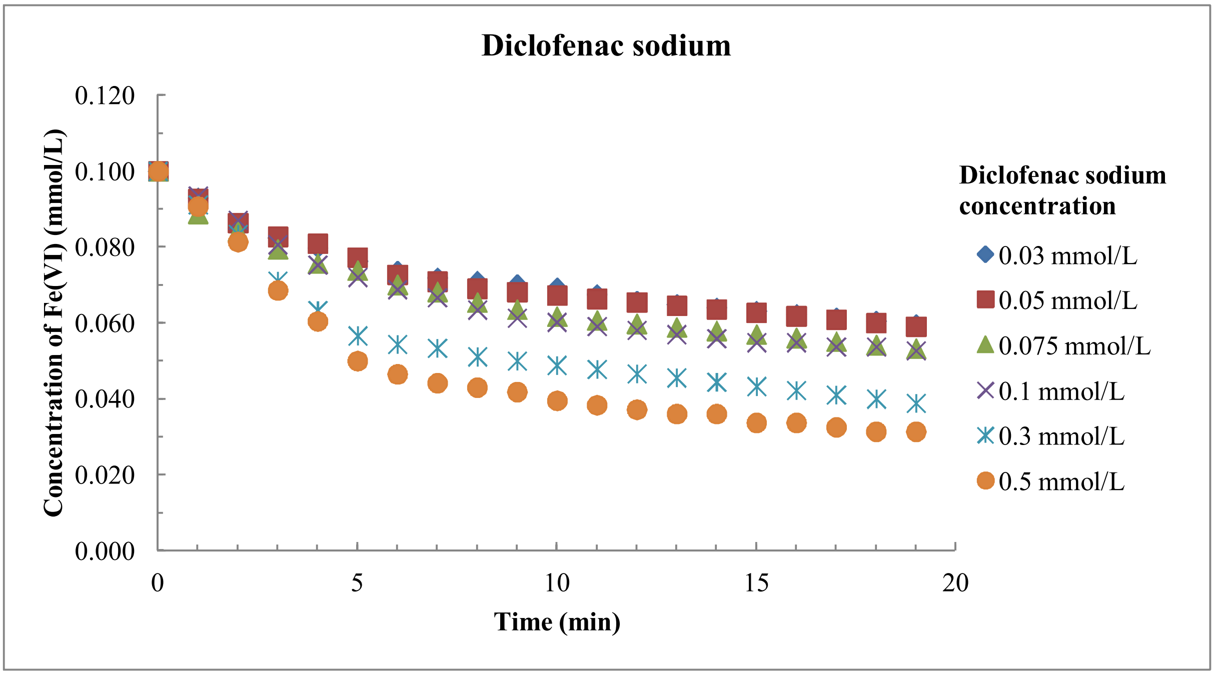


Figure 3.11 Degradation of diclofenac sodium as a function of time for different concentration of diclofenac sodium at a constant ferrate(VI) dose of 0.1 mmol/L and at constant pH 8.0.

3.2.1.2.Kinetics of ferrate(VI) degradation

Further, the kinetics of the degradation of diclofenac sodium was obtained using the time dependence change in concentration of ferrate(VI) at neutral pH 7.0. The rate expression of ferrate(VI) reduction in presence of diclofenac sodium could be written as :

$$-\frac{d[Fe(VI)]}{dt} = k_{app}\ [Fe(VI)]^m\ [Diclofenac\ \ sodium\ ]^n \qquad \ldots(3.5)$$

where k_{app} is the apparent rate constant of the degradation of ferrate(VI) in presence of diclofenac sodium. Further, at varied concentrations of the diclofenac sodium, the above equation is reduced to :

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)]^m \qquad \ldots(3.6)$$

where, $k = k_{app}$ [Diclofenac sodium]^n ...(3.7)

Using the time dependence change in ferrate(VI) concentration obtained at UV_{510}, the data was utilized to fit into the pseudo-first-order rate and pseudo-second-order rate equations as to optimize the value of ‘m’ either 1 or 2. It was observed that the kinetic data was reasonably fitted well to the pseudo-second order rate kinetics and indicated that the value of ‘m’ was 2 with respect to the degradation of ferrate(VI) in presence of diclofenac sodium. Therefore, the pseudo-second order rate constant values at different concentrations of diclofeanc sodium were estimated and returned in table 3.6 with the regression coefficient (R^2). It is clearly observed that increasing the diclofenac sodium concentration (from 0.03 to 0.5 mmol/L) was caused significantly to increase the pseudo-second order rate constant values. This was due to the fairly high oxidizing capacity of ferrate(VI) towards the pollutants which enabled more and more oxidation of the pollutant species in aqueous solutions (García-Araya *et al.*, 2010).

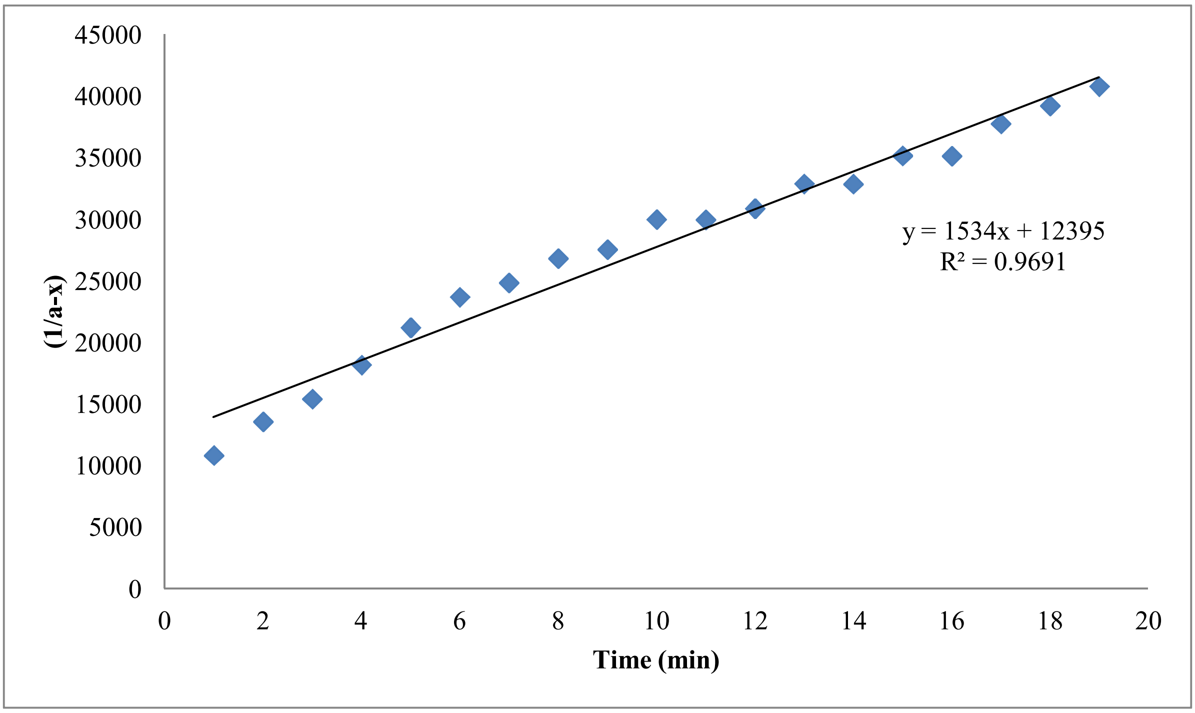


Figure 3.12 Pseudo second order rate kinetics for ferrate(VI) in presence of diclofenac sodium at pH 7.0 Initial [Fe(VI)] : 0.1 mmol/L and [Diclofenac sodium] : 0.1 mmol/L)

Table 3.6 Pseudo-second order rate constant values estimated in the degradation of ferrate(VI) in presence of diclofenac sodium at pH 7.0.

Ferrate(VI) concentration (mmol/L)	**Diclofenac sodium concentration (mmol/L)**	**Pseudo-second order rate constant k (L/mol/min)**	**R^2**
0.1	0.03	1302.9	0.960
0.1	0.05	1370.5	0.971
0.1	0.075	1543.2	0.968
0.1	0.1	1534	0.969
0.1	0.3	5941.3	0.970
0.1	0.5	7487.6	0.942

Further, the value of 'n' along with the apparent rate constant value k_{app} was estimated using the pseudo-second rate constant values obtained at varied concentration of diclofenac sodium at pH 7.0. The plots were drawn between the concentrations of diclofenac sodium against the estimated k values and returned in figure 3.13. The data was reasonably fitted well and hence the value of n was found to be 1. Therefore, the stoichiometric ratio of the ferrate(VI) and diclofenac sodium was found to be 2:1. Moreover, the overall rate constant k_{app} was estimated to be 1458.4 L/mol/min at pH 7.0. Previously, it was reported the degradation of E2, EE2 and bisphenol A was followed the second order rate law and the rate constant values were ranged from the 6.4×10^2 to 7.7×10^2 L/mol/s at pH 7.0 (Lee *et al.*, 2005).

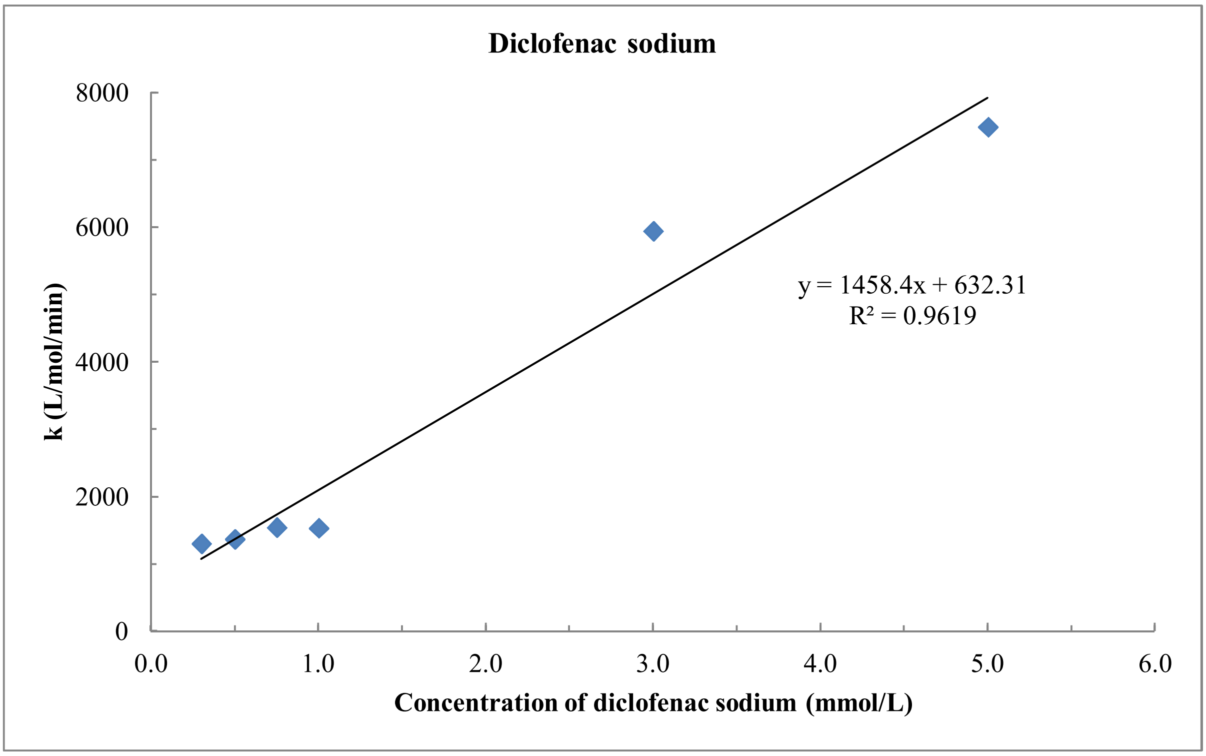


Figure 3.13 Variation of pseudo-second-order rate constants (k) values as a function of diclofenac sodium concentration at pH 7.0.

3.2.2. Removal of diclofenac sodium using HPLC measurements

The diclofenac sodium concentration was determined using the high performance liquid chromatography (HPLC). The HPLC analysis was conducted using the C18 column (5 µm particle size, 250 mm length, and 4.6 mm inner diameter) with mobile phase of acetonitrile : water : acetic acid (70:29:1, v/v/v). The flow rate of mobile phase was maintained to 0.5 mL/min. An injection volume of 20 µl was used and the concentration of diclofenac was determined using the UV detector at 276 nm wavelength. The standard calibration curve of diclofeanc sodium was obtained and the chromatogram showed that the diclofenac sodium was appeared at the retention time 11.78 minute. The HPLC chromatogram, i.e. peak area was calculated using EMPOWER2 Software in µV*sec unit which corresponds to the concentration of diclofenac sodium in an aqueous solution. The concentration of diclofenac sodium was varied from 0.03 mmol/L to 0.5 mmol/L whereas the concentration of ferrate(VI) was kept constant at 0.1 mmol/L. Therefore, the Fe(VI) : BPA molar ratio was maintained as 1:0.3, 1:0.5, 1:0.75, 1:1, 1:3 and 1:5. All these different molar concentrations were studied separately at varied pH conditions i.e., pH 7.0 to 12.0. The diclofenac sodium peak area and the ferrate(VI) treated diclofenac sodium sample area was used to obtain the percent removal of diclofenac sodium from solutions. It was found that 65% of diclofenac sodium was removed at the 0.1 mmol/L of ferrate(VI) and 0.03 mmol/L of diclofenac concentration at pH 7.0 as shown in the table 3.7. The removal of diclofenac sodium was decreased as the concentration of diclofenac sodium was increased. High percent removal of diclofenac was obtained at pH 7.0 because the reactivity of ferrate(VI) was enhanced at lower pH values. The percent removal was decreased as the pH of the aqueous solution was increased from pH 7.0 to 12.0. At pH 7.0, in the Fe(VI) : Diclofenac sodium molar ratio 1:1, the percent removal was 41% and the overlay peaks of diclofenac (red) and diclofenac treated with ferrate(VI) (green) was shown in the figure 3.15. It is interesting to note that no additional peak was observed at this wavelength suggesting no other by-product formation of the diclofenac sodium in aqueous solution.

Table 3.7 Percent removal of diclofenac sodium by ferrate(VI) at different pH and molar ratios of diclofenac sodium with ferrate(VI).

pH	Initial concentration (mmol/L)		Area (µV*sec)	% Removal
	Ferrate(VI)	Diclofenac sodium		
7.0	0	0.03	2807586	65.00
	0.1	0.03	982655	
	0	0.05	4474317	60.00
	0.1	0.05	1789726	
	0	0.075	6199552	47.00
	0.1	0.075	3285762	
	0	0.1	8367772	41.00
	0.1	0.1	4936985	
	0	0.3	23916171	26.00
	0.1	0.3	17697966	
	0	0.5	39508798	21.00
	0.1	0.5	31211950	
8.0	0	0.03	2189685	61.32
	0.1	0.03	846970	
	0	0.05	4805000	56.91
	0.1	0.05	2070316	
	0	0.075	5476385	45.17
	0.1	0.075	3002701	
	0	0.1	8386196	41.62
	0.1	0.1	4895990	
	0	0.3	21932583	24.06
	0.1	0.3	16655603	
	0	0.5	41658426	18.48
	0.1	0.5	33958238	
9.0	0	0.03	2157693	58.25
	0.1	0.03	900836	
	0	0.05	4442742	52.01
	0.1	0.05	2131987	
	0	0.075	5378943	42.38
	0.1	0.075	3099346	
	0	0.1	8514936	38.93
	0.1	0.1	5200167	
	0	0.3	22481976	21.67
	0.1	0.3	17610131	
	0	0.5	41975523	16.15
	0.1	0.5	35196994	

pH	**Initial concentration (mmol/L)**		**Area (µV*sec)**	**% Removal**
	Ferrate(VI)	**Diclofenac sodium**		
10.0	0	0.03	2213654	47.42
	0.1	0.03	1163939	
	0	0.05	4272678	40.57
	0.1	0.05	2539280	
	0	0.075	5356783	36.24
	0.1	0.075	3415484	
	0	0.1	8220215	31.30
	0.1	0.1	5647155	
	0	0.3	21437587	19.21
	0.1	0.3	17319426	
	0	0.5	41242687	15.28
	0.1	0.5	34940804	
11.0	0	0.03	2215843	24.48
	0.1	0.03	1673404	
	0	0.05	4155904	19.14
	0.1	0.05	3360463	
	0	0.075	5234674	17.23
	0.1	0.075	4332739	
	0	0.1	8536472	14.78
	0.1	0.1	7274390	
	0	0.3	22547894	12.62
	0.1	0.3	19702349	
	0	0.5	40587354	10.80
	0.1	0.5	36203628	
12.0	0	0.03	2123521	20.31
	0.1	0.03	1692233	
	0	0.05	4230797	17.23
	0.1	0.05	3501830	
	0	0.075	5312453	15.45
	0.1	0.075	4491679	
	0	0.1	8512251	13.54
	0.1	0.1	7359692	
	0	0.3	22438795	11.76
	0.1	0.3	19799992	
	0	0.5	40921364	9.95
	0.1	0.5	36849688	

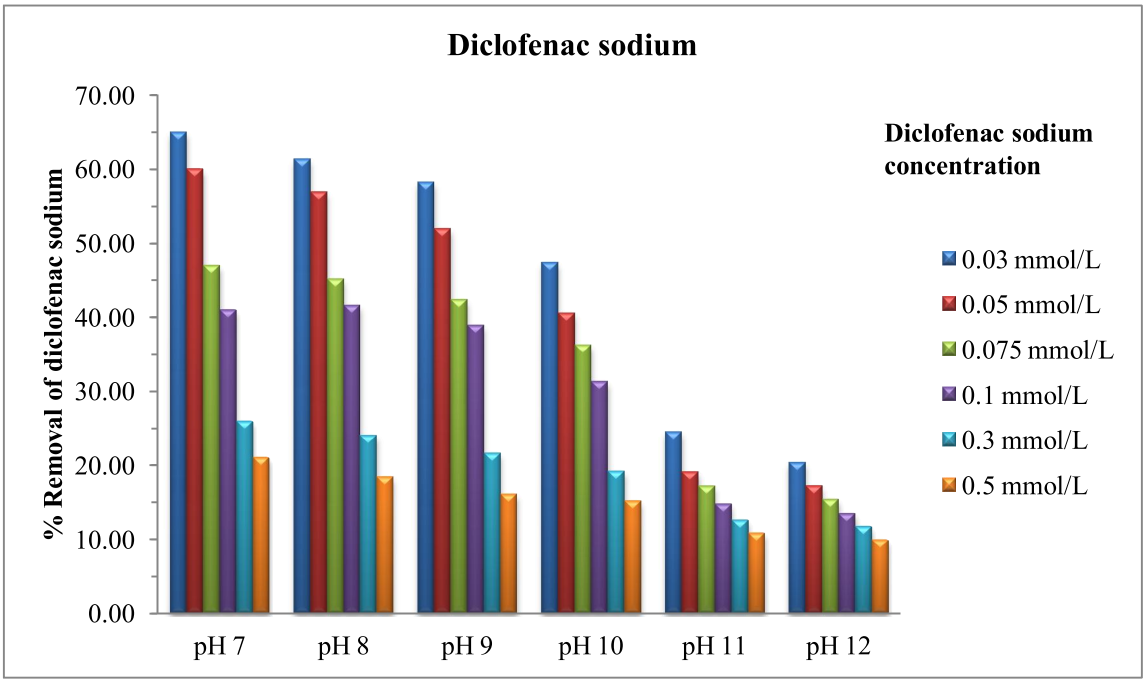


Figure 3.14 Percent removal of diclofenac sodium at different concentrations of DCF and various pH values. [Fe(VI) dose : 0.1 mmol/L)

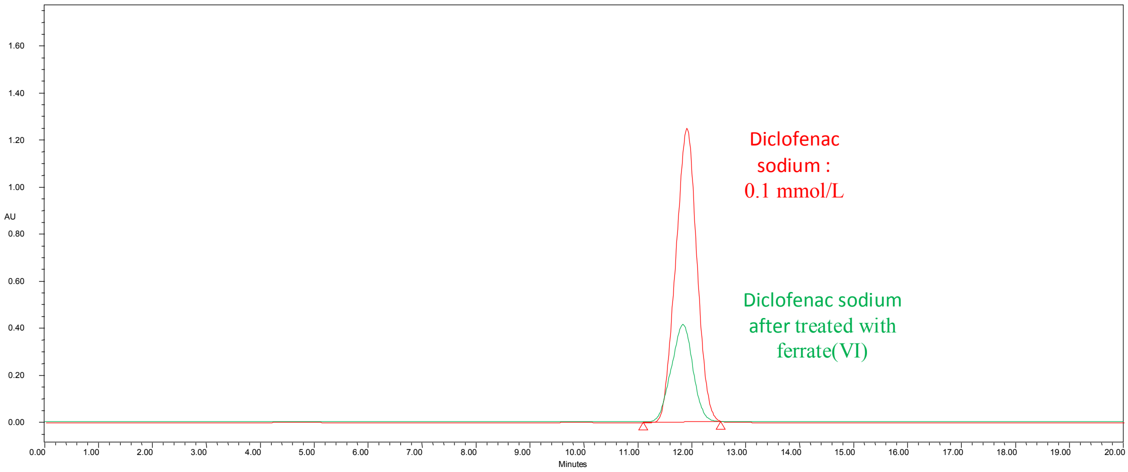


Figure 3.15 Degradation of diclofenac sodium at ferrate(VI) : diclofenac molar ratio 1:1 (pH 7.0).

3.2.3. Effect of pH in the degradation of diclofenac sodium by ferrate(VI)

The pH dependence study is an useful parameter in order to optimize the selectivity of solution pH to degrade the diclofenac sodium from aqueous solutions. Additionally, it provides the mechanism involved in the degradation of pollutant with ferrate(VI). The degradation of diclofenac sodium was further studied using the HPLC measurements and the results are returned in figure 3.14 as percent removal of diclofenac sodium against the solution pH and concentration of micro-pollutant. It was observed in general that increasing the concentration of diclofenac sodium caused to decrease in percent removal of DCF at a constant dose of ferrate(VI). More quantitatively, increasing the concentration of DCF from 0.03 to 0.5 mmol/L the corresponded decrease in percent removal of DCF was found to be from 65.0% to 21.0%, respectively at pH 7.0 and at ferrate(VI) dose of 0.10 mmol/L. This decrease in percent removal was primarily due to the fact that at lower concentration of diclofenac sodium relatively more number of ferrate(VI) molecules were present to degrade the lesser number of DCF molecules. However, increasing the concentration of DCF an apparent increase in content of DCF removal was obtained. This indicated that although at lower concentration the percent removal of Diclofenac sodium was higher however, the increase in pollutant concentration favoured the content removal of pollutant at constant dose of ferrate(VI).

On the other hand the decrease in pH from pH 12.0 to 7.0 enabled to increase significantly the percent removal of diclofenac sodium from aqueous solutions (*cf* figure 3.14). Quantitatively, decreasing the pH from 12.0 to 7.0 the corresponding percent degradation of BPA was increased from 13.54 to 41% at the ferrate(VI) to Diclofenac molar ratio 1:1. It was reported previously that at pH 7.0 the protonated species of the ferrate(VI) i.e., $HFeO_4^-$ dominated in aqueous solutions since the pK_a value for the acid dissociation of $HFeO_4^-$ was reported to be 7.3 (Sharma *et al.*, 2001). Moreover, the protonated species of ferrate(VI) was found to possess an enhanced reactivity and caused for an enhanced degradation of DCF in aqueous solution (Ohta *et al.*, 2001; Sharma *et al.*, 2004). Previously it was reported in a line that the higher degradation was reported with the protonated species of ferrate ($HFeO_4^-$) than the deprotonated species (FeO_4^{2-}) in the degradation of diclofenac from aqueous solutions (Li *et al.*, 2008).

3.2.4. Mineralization of Diclofenac sodium

Further, it is interesting to obtain the mineralization of diclofenac sodium with ferrate(VI) treatment. The samples of diclofenac sodium having varied concentrations (0.03 to 0.5 mmol/L) were treated with a constant dose of ferrate(VI) for a period of 2 hrs at constant but at varied pH conditions (pH 7.0 to 12.0) and then the samples were subjected for the estimation of the total TOC (total organic carbon) values. The untreated samples of diclofenac sodium were also measured as the initial TOC values. Using the TOC measurements the percent TOC removal of the DCF was obtained (Table 3.8) and presented as a function of pollutant concentration and solution pH in figure 3.16(a). It is evident from the figure 3.16(a) that the decrease in BPA concentration and pH favoured greatly the percent removal of TOC. Quantitatively, decreasing the BPA concentration from 0.5 to 0.03 mmol/L caused to increase the TOC removal from 10.32% to 38.25% as observed at pH 7.0. Similarly, decreasing the solution pH from 12.0 to 7.0 the corresponding increase in percent TOC removal was found to be 2.37% to 16.63% at the 1:1 molar ratio of the ferrate(VI) to Diclofenac sodium. The trend of this result is in a line to the kinetic and HPLC results obtained previously. It is also evident from the TOC data that although a partial mineralization of DCF was obtained but a significant percent mineralization was recorded using a single dose of ferrate(VI).

On the other hand the data was further presented in terms of total amount of the DCF mineralized by the ferrate(VI) treatment and were presented as a function of DCF initial concentration and solution pH (*cf* figure 3.16(b)) . It is interesting to observe that increasing the concentration of DCF was favoured significantly the content removal of DCF from aqueous solutions. Whereas the decrease in pH (i.e., from pH 12.0 to 7.0) favoured the content removal of DCF.

Table 3.8 Mineralisation of diclofenac sodium by ferrate(VI) at different pH and Diclofenac concentrations (Fe(VI) concentration 0.1 mmol/L)

pH	**% Mineralisation of diclofenac sodium by ferrate(VI) treatment**					
	[Fe(VI)] : [Diclofenac sodium]					
	1:0.3	**1:0.5**	**1:0.75**	**1:1**	**1:3**	**1:5**
7.0	38.25	36.38	20.24	16.63	13.42	10.23
8..0	30.39	27.35	14.54	10.97	9.36	8.27
9.0	24.03	21.44	16.71	9.15	7.28	6.26
10.0	23.82	20.59	15.49	8.88	7.06	5.61
11.0	20.00	16.31	9.01	7.19	5.85	4.78
12.0	12.36	7.84	6.69	2.37	3.12	4.41

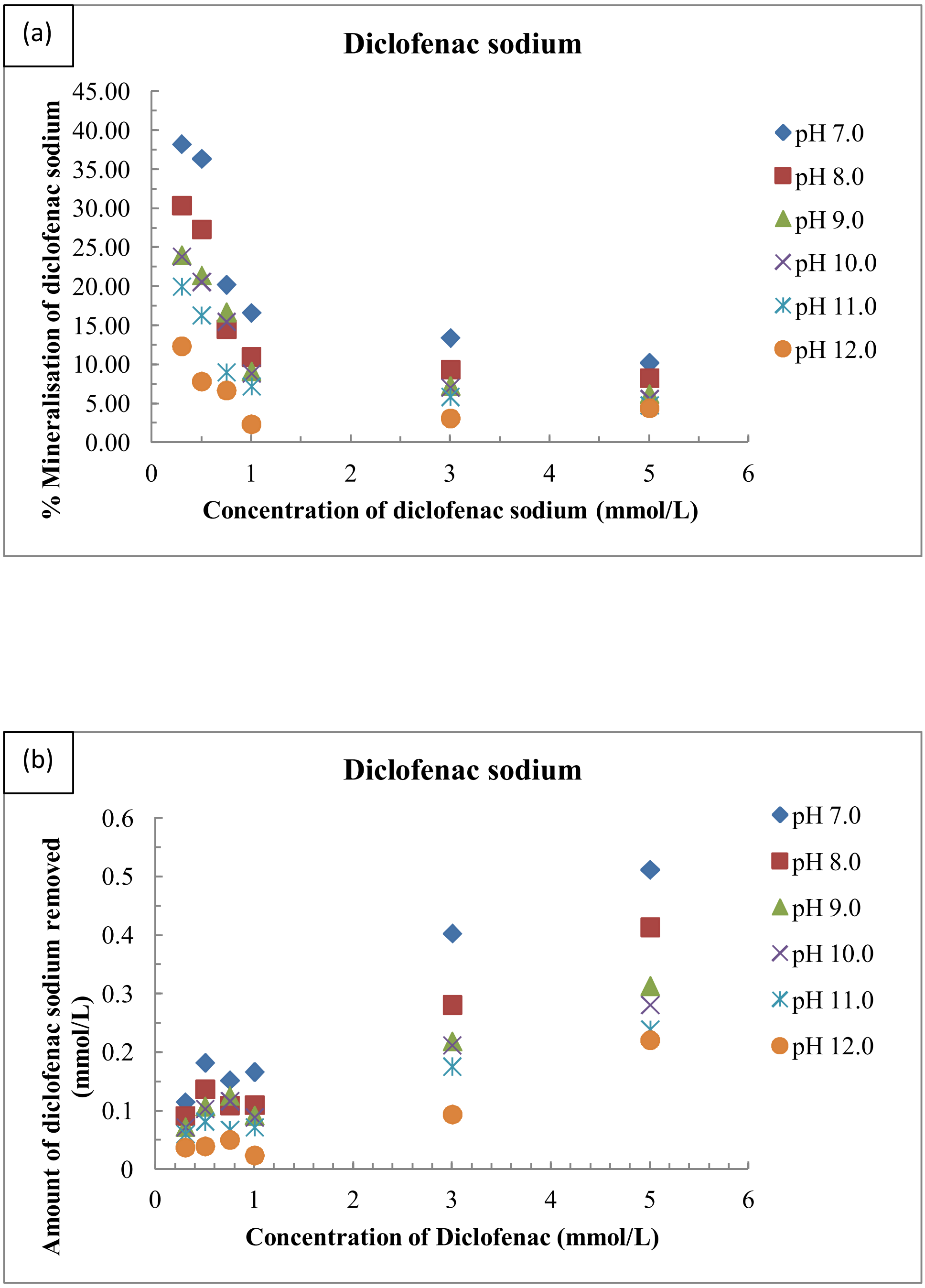


Figure 3.16 (a) Percent mineralisation; and (b) extent removal of diclofenac sodium as a function of pH and diclofenac sodium concentrations at a constant dose of ferrate(VI) : 0.1 mmol/L.

3.2.5. Effect of background electrolytes

The presence of co-exiting ions in the oxidative removal of DCF (0.1 mmol/L) was studied using the ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3 were used as co-existing ions. Variety of electrolytes was used having partly or fully oxidized ions in order to assess the suitability of ferrate(VI) towards the DCF degradation in aqueous solutions. The results are returned graphically in figure 3.17. Results indicated that the presence of fully oxidized electrolytes *viz.*, NaCl, $NaNO_3$ and Na_2HPO_4 could not affect the oxidation of DCF by ferrate(VI). It is to be noted that presence of phosphate and nitrate caused to increase slightly the degradation of DCF. This was possibly due to the fact that ferrate(VI) was relatively stable in the phosphate media forming complexes with Fe(III) otherwise forming precipitates of iron oxide which accelerated the spontaneous fast decomposition of ferrate(VI) (Thompson *et al.*, 1951). However, on the other hand the partly oxidized $NaNO_2$ and Na_2SO_3 were caused upto a lower extent the decrease in the decomposition of DCF from aqueous solutions. Previously, it was reported that the presence of NO_2^- and SO_3^- greatly affected the degradation of the Zn(II)-NTA complex by the ferrate(VI) since the ferrate(VI) decomposition was increased significantly in presence of these electrolytes (Yang *et al.*, 2010). Further, the extent of oxidation of DCF by the ferrate(VI) was studied increasing the $NaNO_2$ or Na_2SO_3 concentration from 0.1 to 5.0 mmol/L at a constant DCF and ferrate(VI) concentration of 1.0 mmol/L and at pH 8.0. The results were returned graphically in figure 3.18. It is evident from the figure that increasing the background concentration from 0.1 to 5.0 mmol/L $NaNO_2$ the corresponding decrease in percent removal of DCF was from 39.06% to 35.95 % (i.e., 3.11% decrease only), respectively. On the other hand, the Na_2SO_3 was caused to decrease the percent removal of DCF from 38.18% to 35.53% (i.e., 2.65% decrease) for the similar increase in electrolyte concentration from 0.1 to 5.0 mmol/L. The insignificant decrease in percent removal of DCF even with increasing the partially oxidized electrolytes *viz.*, $NaNO_2$

and Na_2SO_3 pointed the affinity and potential application of ferrate(VI), at least, in the degradation of DCF from aqueous solutions.

Table 3.9 Percent removal of diclofenac sodium by ferrate(VI) as a function of different background electrolytes at pH 8.0. (HPLC measurement) (Blank = 41.62% removal)

Electrolyte	**Area(µV*sec)**		**% Removal**
	Diclofenac sodium	**Diclofenac sodium + Electrolyte + Ferrate(VI)**	
Na_2HPO_4	8386196	4791033	42.87
Na_2SO_4	8386196	4893345	41.65
$NaNO_3$	8386196	4820385	42.52
NaCl	8386196	4832126	42.38
$NaNO_2$	8386196	5110547	39.06
Na_2SO_3	8386196	5184346	38.18

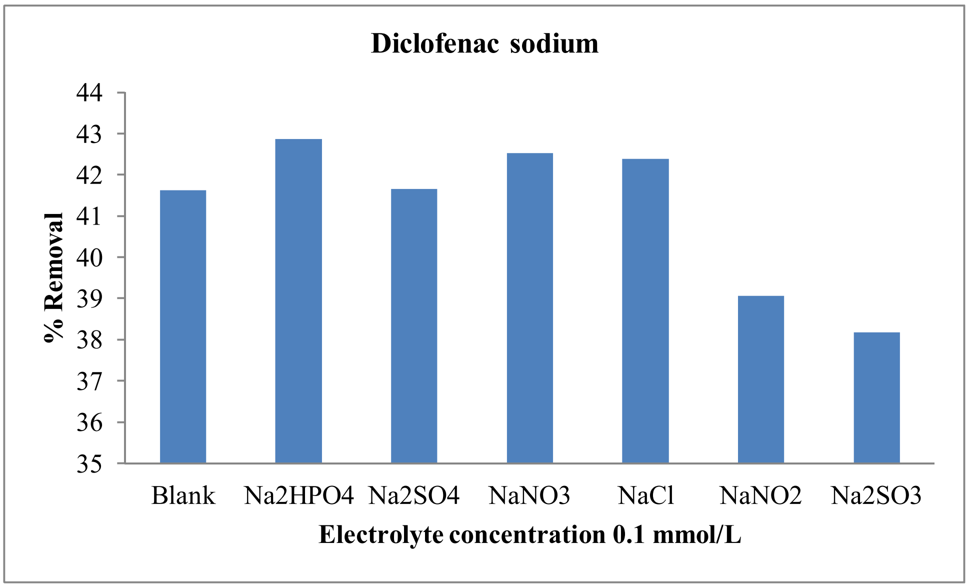


Figure 3.17 Effect of electrolytes in the degradation of diclofenac sodium by ferrate(VI) at pH 8.0.

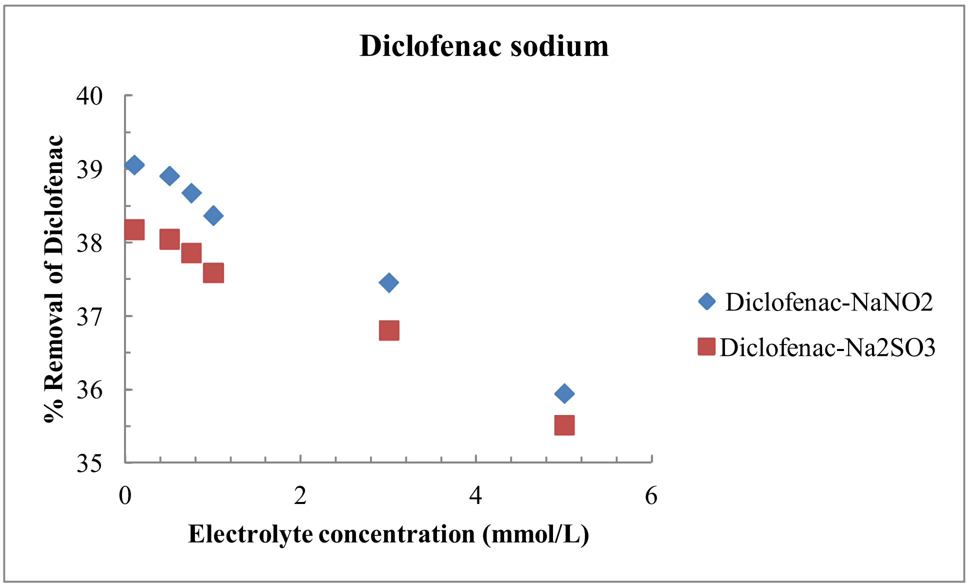


Figure 3.18 Effect of various concentrations of electrolyte in the degradations of diclofenac sodium by ferrate(VI).

Similar to HPLC measurements, the mineralization of DCF by ferrate(VI) was assessed in presence of several electrolytes *viz*., Na_2HP_4, Na_2SO_4, NaCl, $NaNO_3$, $NaNO_2$ and Na_2SO_3. The total organic carbon data was collected in presence of these electrolytes and with the help of blank data the percent TOC removal was calculated and returned in Table 3.10 and graphically presented in Figure 3.17. It is interesting to note that a partial % TOC removal was almost unaffected in presence of Na_2PO_4, Na_2SO_4, $NaNO_3$ and NaCl. However, a small but insignificant decrease of DCF % mineralization was occurred in presence of $NaNO_2$ and Na_2SO_3. These results are in a line to the HPLC measurements of total DCF removal by ferrate(VI) in presence of these electrolytes. Further, the concentration of $NaNO_2$ and Na_2SO_3 was increased from 0.1 to 5.0 mmol/L while DCF and ferrate(VI) concentration was kept constant 0.1 mol/L each and solution was maintained at pH 8.0. The % TOC removal of DCF as a function of electrolyte concentrations was presented graphically in Figure 3.20. It is further found that the percent TOC removal of DCF was not much affected even increasing the electrolyte concentration (i.e., $NaNO_2$ and Na_2SO_3) to 5.0 mmol/L.

Table 3.10 Percent mineralization of diclofenac sodium by ferrate(VI) as a function of different background electrolytes at pH 8.0. (TOC measurements) (Blank = 10.97% mineralization)

Electrolyte	**Total Organic Carbon (mg/L)**		**% Mineralisation**
	Diclofenac sodium	**Diclofenac sodium + electrolyte + Ferrate(VI)**	
Na_2HPO_4	15.04	13.42	10.77
Na_2SO_4	15.04	13.4	10.90
$NaNO_3$	15.04	13.43	10.70
NaCl	15.04	13.41	10.84
$NaNO_2$	15.04	13.66	9.18
Na_2SO_3	15.04	13.72	8.78

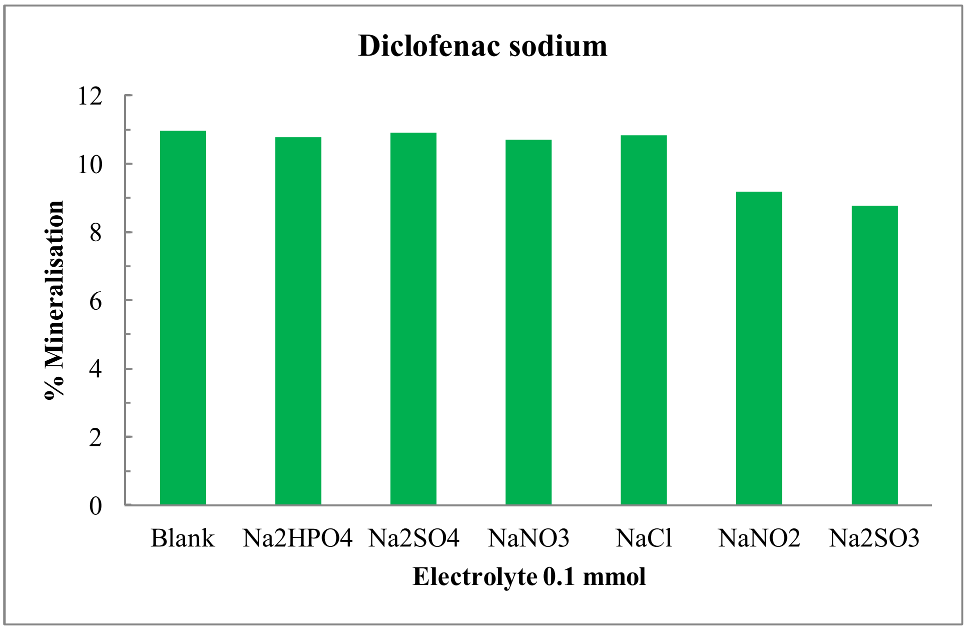


Figure 3.19 Effect of electrolytes in the mineralization of diclofenac by ferrate(VI) at pH 8.0.

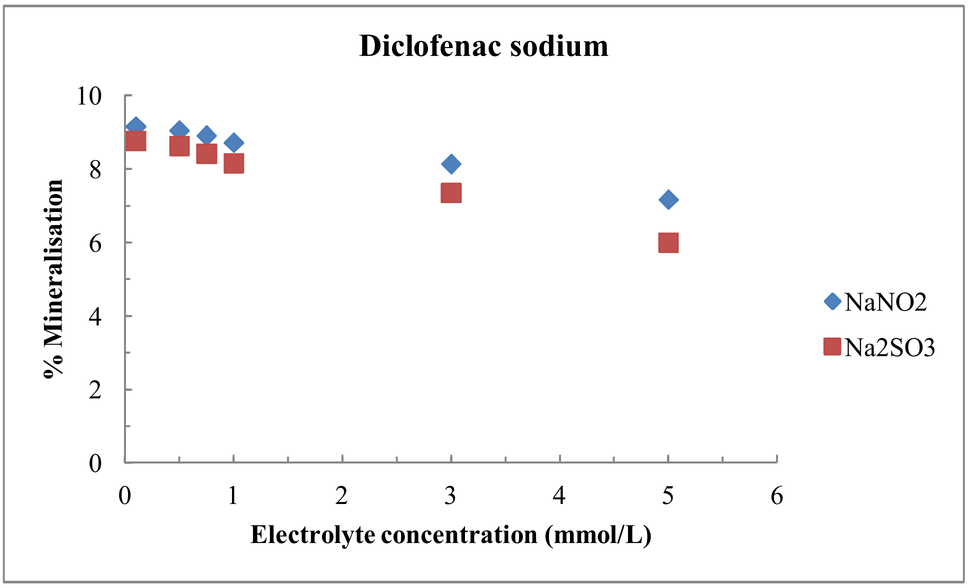


Figure 3.20 Effect of various concentrations of electrolytes $NaNO_2$ and Na_2SO_3 in the mineralization of diclofenac sodium by ferrate(VI).

3.3. 17α-ethynylestradiol (EE2)

3.3.1. Degradation of 17α-ethynylestradiol (EE2) species using UV-Vis measurements

3.3.1.1. Effect of concentration of 17α-ethynylestradiol (EE2)

The 17α-ethynylestradiol (EE2) micro-pollutant was treated with ferrate(VI) under the simulated batch reactor operations. The molar ratios of ferrate(VI) to EE2 was varied from 1:0.3 to 1:5 and the treatment pH was varied from pH 7.0 to 12.0. The 17α-ethynylestradiol (EE2) concentration was taken from 0.03 mmol/L to 0.3 mmol/L at a constant ferrate(VI) dose of 0.1 mmol/L. The results are presented graphically in figure 3.21 for the change in ferrate(VI) concentration in presence of 17α-ethynylestradiol (EE2) (pH 8.0 is taken as representative graph). It is evident from the figure that increasing the concentration of 17α-ethynylestradiol (EE2) the reduction of ferrate(VI) was increased sharply. Therefore, the degradation of the pollutants were increased significantly with the increase in pollutant concentration at a constant dose of ferrate(VI). Further, it was observed that the ferrate(VI) concentration was decreased sharply during the initial period of contact followed by an apparent equilibrium or the constant concentration of ferrate(VI) was obtained. The maximum decrease of ferrate(VI) concentration was observed within initial *Ca* 5 minutes of contact in presence of this pollutant. This showed the potential use of ferrate(VI) in the degradation of pollutants from aqueous solutions. Quantitatively, increasing the contact time from 0 to 20 min the amount of ferrate(VI) was decreased from 0.10 to 0.011 mmol/L for 17α-ethynylestradiol(EE2) in the 1:1 molar ratios of ferrate(VI) and pollutant concentration.

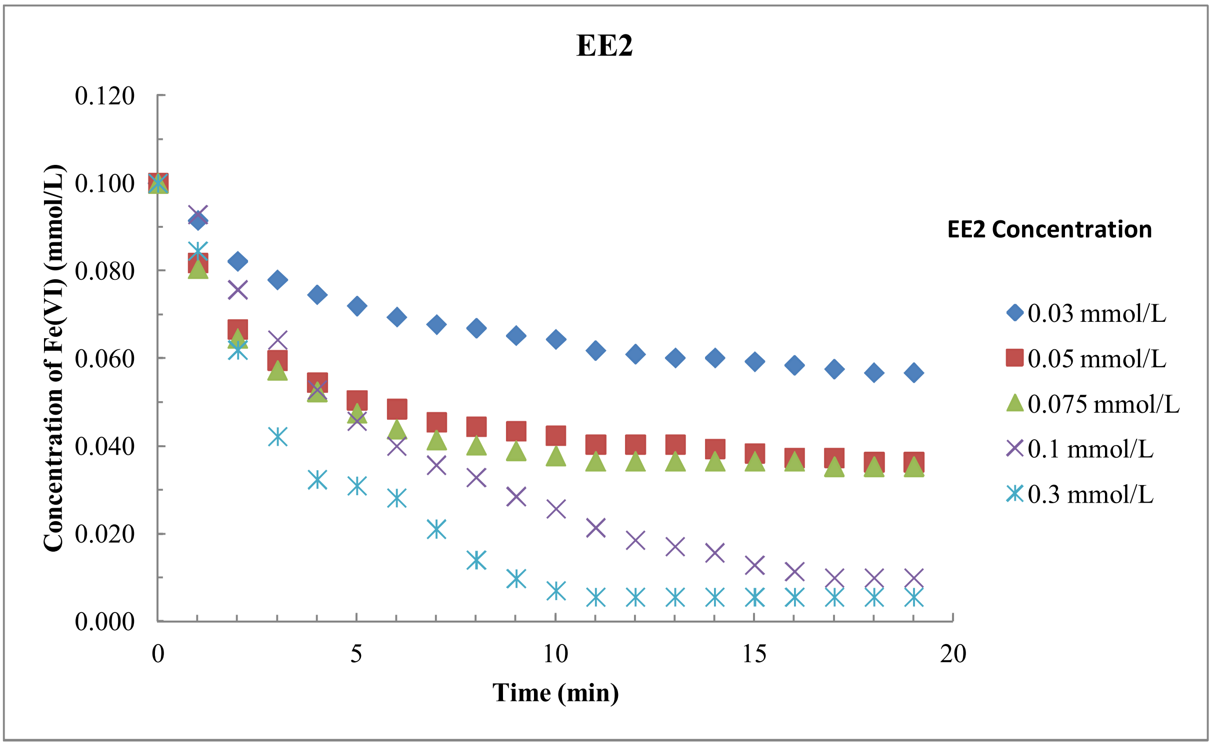


Figure 3.21 Degradation of 17α-ethynylestradiol (EE2) as a function of time for diferrent concentration of 17α-ethynylestradiol (EE2) for the constant ferrate(VI) dose of 0.1 mmol/L ferrate(VI) at constant pH 8.0.

3.3.1.2. Kinetics of ferrate(VI) degradation

Further, the kinetics of the degradation of 17α-ethynylestradiol (EE2) was discussed using the time dependence change in ferrate(VI) concentration at neutral pH 7.0. The absorbance data is corrected for the self-decomposition of ferrate(VI) using the blank run and then normalized to the ferrate(VI) concentration. Further, this was utilized in the rate calculations. It was earlier reported that the decomposition of ferrate(VI) into Fe(III) occurred through the following reductive pathways (Pachuau *et al.*, 2013; Zhang *et al.*, 2012):

$$2FeO_4^{2-} + 3H_2O \rightarrow 2\,Fe(OH)_3 + 5[O] \quad \ldots(3.8)$$

$$[O] + H_2O \rightarrow 2\,{\bullet}OH \quad \ldots(3.9)$$

$$2\,{\bullet}OH \rightarrow H_2O2 \quad \ldots(3.10)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \ldots.(3.11)$$

With this the hydroxyl free radical generated is one of strong oxidizing agent (Han *et al.*, 2013) which may likely to oxidize the pollutants in aqueous solutions. The simple kinetics in the degradation of EE2 is discussed by the change in ferrate(VI) concentrations using the absorbance data collected at 510 nm wave length. The basic equation for the reduction of ferrate(VI) in presence of EE2 may be represented as:

$$Fe(VI) + EE2 \rightarrow Fe(III) + \text{Oxidized Products} + CO_2 \quad \ldots(3.12)$$

It was assumed that partly/or fully the EE2 was mineralized to its end products, which is analyzed by the TOC values. Moreover, the self-decomposition of ferrate(VI) was even significant at the studied pH values (Tiwari *et al.*, 2007; Lee *et al.*, 2004). Therefore, the necessary blank correction was conducted at the same pH conditions. The rate expression of ferrate(VI) reduction in presence of 17α-ethynylestradiol (EE2) could be written as in equation (3.12):

$$-\frac{d[Fe(VI)]}{dt} = \text{kapp}\ [Fe(VI)]^m\ [EE2]^n \quad \ldots(3.13)$$

where k_{app} is the apparent rate constant of the degradation of ferrate(VI) in presence of 17α-ethynylestradiol (EE2). Further, at varied concentration of the 17α-ethynylestradiol (EE2), the above equation could be reduced to equation (3.13)

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)]^{m} \qquad \ldots(3.14)$$

where, $k = k_{app}\,[EE2]^{n}$ …(3.15)

The time dependence ferrate(VI) concentration data was utilized to fit into the pseudo-first-order rate and pseudo-second-order rate equations as to optimize the value of 'm' either 1 or 2. It was observed that the kinetic data was reasonably fitted well to the pseudo-second order rate kinetics and indicated that the value of m was '2' with respect to the degradation of ferrate(VI) in presence of 17α-ethynylestradiol (EE2). Therefore, the pseudo-second order rate constant values were estimated and returned in table 3.11 with the regression coefficient (R^2). It was clearly observed that increasing the 17α-ethynylestradiol (EE2) concentration (from 0.03 to 0.3 mmol/L) was caused significantly to increase the pseudo-second order rate constant values. This was due to the fairly high oxidizing capacity of ferrate(VI) towards the pollutants which enabled more and more oxidation of the pollutant species in aqueous solutions (García- Araya *et al*., 2010).

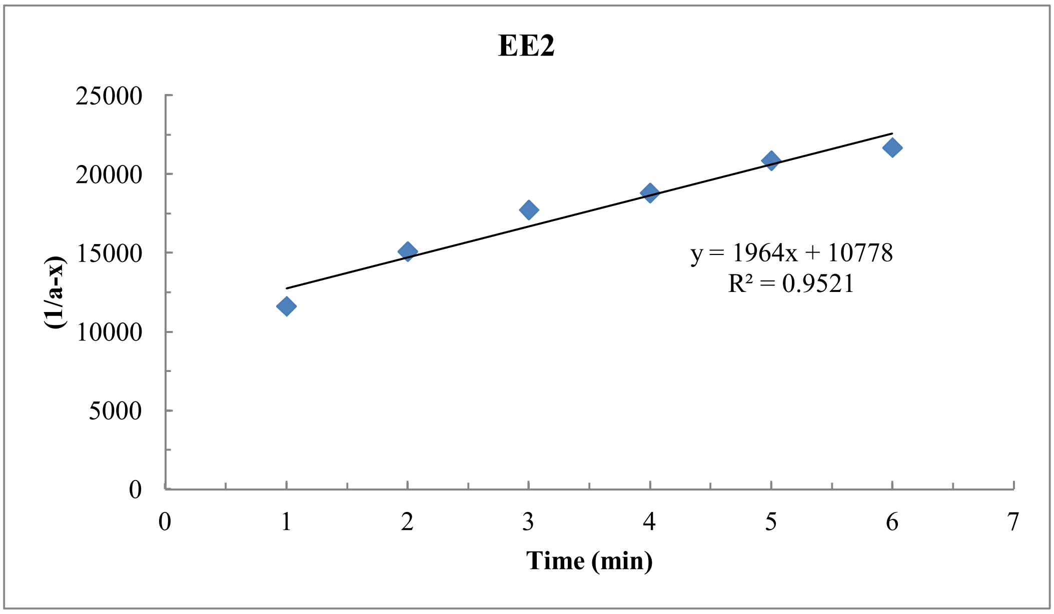


Figure 3.22 Pseudo second order rate kinetics for ferrate(VI) in presence of 17α-ethynylestradiol (EE2) at pH 7.0 ([Fe(VI)] : 0.1 mmol/L; [17α-ethynylestradiol (EE2)] : 0.1 mmol/L)

Table 3.11 Pseudo-second order rate constants estimated in the degradation of ferrate(VI) in presence of 17α-ethynylestradiol (EE2) at pH 7.0.

Ferrate(VI) concentration (mmol/L)	17α-ethynylestradiol (EE2) concentration (mmol/L)	Pseudo-second order rate constant k (L/mol/min)	R^2
0.1	0.03	548.27	0.926
0.1	0.05	1497	0.970
0.1	0.075	1676.1	0.984
0.1	0.1	1964	0.952
0.1	0.3	4244.7	0.992

Further, the value of ‘n’ along with the apparent rate constant value k_{app} was estimated using the pseudo-second rate constant values obtained at varied concentration of 17α-ethynylestradiol (EE2) at pH 7.0. The plots were drawn between the concentrations of 17α-ethynylestradiol (EE2) against the estimated k values and returned in figure 3.23. It is clearly demonstrated that the data was reasonably fitted well and hence the value of ‘n’ was found to be 1. Therefore, the stoichiometric ratio of the ferrate(VI) and 17α-ethynylestradiol (EE2) was found to be 2:1. Moreover, the overall rate constant k_{app} was estimated to be 12328 L/mol/min at pH 7. Previously, it was reported the degradation of E2, EE2 and bisphenol A was followed the second order rate law and the rate constant values were ranged from the $6.4x10^2$ to $7.7x10^2$ L/mol/s at pH 7.0 (Lee *et al.*, 2005). It was previously reported that the ferrate(VI) to bisphenol A (BPA) molar ratio 5:1 may enable to degrade completely the BPA. Moreover, it was also concluded that the molar ratio of ferrate to several EDCs in practice is several orders of magnitude (Li *et al.*, 2008). The other studies showed that the decomposition of N-nitrosodimethylamine (NDMA) precursors to (dimethyldithiocarbamate, dimethylaminobenzene, 3-(dimethylaminomethyl)indole and 4-dimethylaminoantipyrine) possessed with high reactivity toward ferrate(VI) with k_{app} values at pH 7 between $2.6x10^2$ and $3.2x10^5$ $M^{-1}s^{-1}$. The other NDMA precursors to (DMA, trimethylamine, dimethylethanolamine, dimethylformamide) and NDMA possessed k_{app} values ranging from 0.55 to 9.1 M^{-1} s^{-1} at pH 7 (Li *et al.*, 2008).

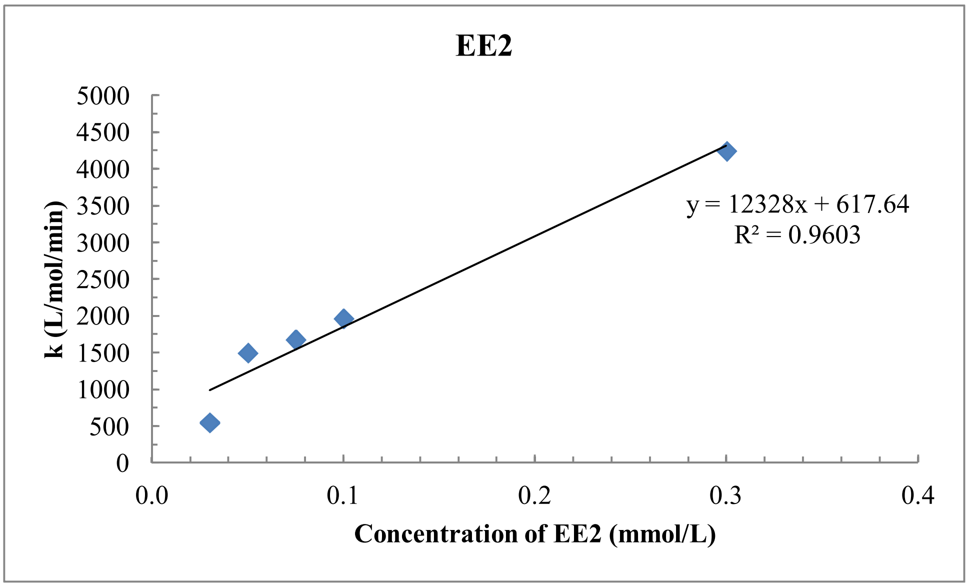


Figure 3.23 Variation of pseudo-second-order rate constants (k) values as a function of 17α-ethynylestradiol (EE2) at pH 7.0.

3.3.2. Oxidative Removal of 17α-ethynylestradiol (EE2) using HPLC measurements

The 17α-ethynylestradiol (EE2) concentration was determined using high performance liquid chromatograph (HPLC). A C18 column (5 µm particle size, 250 mm length, and 4.6 mm inner diameter) was employed and a mobile phase of acetonitrile: water: acetic acid (70:29:1, v/v/v) was used at a flow rate of 1 mL/min. An injection volume of 20 µl was used and the concentration of 17α-ethynylestradiol (EE2) was determined using a UV detector at 280 nm. A standard calibration curve of 17α-ethynylestradiol (EE2) was obtained and the EE2 was appeared at the retention time 3.78 minute. The chromatogram peak area was calculated using EMPOWER2 Software in µV*sec unit which corresponds to the concentration of 17α-ethynylestradiol (EE2) in the aqueous solution. The initial concentration of 17α-ethynylestradiol (EE2) was varied from 0.03 mmol/L to 0.1 mmol/L whereas the concentration of ferrate(VI) was kept constant at 0.1 mmol/L. The Fe(VI) : 17α-ethynylestradiol (EE2) molar ratio was therefore varied from 1:0.3, 1:0.5, 1:0.75, and 1:1. All these samples were studied separately varying the solution pH from pH 7.0 to 12.0. The blank

EE2 peak area was used to estimate the percent removal of EE2 from aqueous solutions. An overlay peak of 17α-ethynylestradiol (EE2) (red) and 17α-ethynylestradiol (EE2) treated with ferrate(VI) (green) as an example is shown in figure 3.25. It was found that 98.73% of 17α-ethynylestradiol (EE2) was removed in the 0.1 mmol/L of ferrate(VI) and 0.03 mmol/L of 17α-ethynylestradiol (EE2) at pH 7 as shown in the Table 3.12. The percent removal of 17α-ethynylestradiol (EE2) was decreased as the concentration of 17α-ethynylestradiol (EE2) was increased. At pH 7.0, in the Fe(VI) : 17α-ethynylestradiol (EE2) molar concentration 1:1, the percent removal was found to be 78.13%.

Table 3.12 Percent Removal of 17α-ethynylestradiol(EE2) species by Fe(VI) at different pH and molar ratio values.

pH	**Initial concentration (mmol/L)**		**Area(μV*sec)**	**% Removal**
	Ferrate(VI)	**EE2**		
7.0	0	0.03	275673	98.73
	0.1	0.03	3501	
	0	0.05	462481	97.79
	0.1	0.05	10220	
	0	0.075	691367	81.01
	0.1	0.075	131290	
	0	0.1	925693	78.13
	0.1	0.1	202449	
8.0	0	0.03	278931	97.96
	0.1	0.03	5690	
	0	0.05	459784	97.81
	0.1	0.05	10069	
	0	0.075	693573	83.12
	0.1	0.075	117075	
	0	0.1	923685	78.45
	0.1	0.1	199054	
9.0	0	0.03	268954	99.22
	0.1	0.03	2097	
	0	0.05	451267	99.09
	0.1	0.05	4106	
	0	0.075	694673	84.34
	0.1	0.075	108785	
	0	0.1	915473	80.36
	0.1	0.1	179798	

pH	**Initial concentration (mmol/L)**		**Area(µV*sec)**	**% Removal**
	Ferrate(VI)	**EE2**		
10.0	0	0.03	261746	99.56
	0.1	0.03	1151	
	0	0.05	452365	99.53
	0.1	0.05	2126	
	0	0.075	686784	92.80
	0.1	0.075	49448	
	0	0.1	914598	87.67
	0.1	0.1	112769	
11.0	0	0.03	267893	98.43
	0.1	0.03	4205	
	0	0.05	468943	97.15
	0.1	0.05	13364	
	0	0.075	694657	90.27
	0.1	0.075	67590	
	0	0.1	926789	85.42
	0.1	0.1	135125	
12.0	0	0.03	269849	98.38
	0.1	0.03	4371	
	0	0.05	457834	96.78
	0.1	0.05	14742	
	0	0.075	683487	89.76
	0.1	0.075	69989	
	0	0.1	917654	82.98
	0.1	0.1	156184	

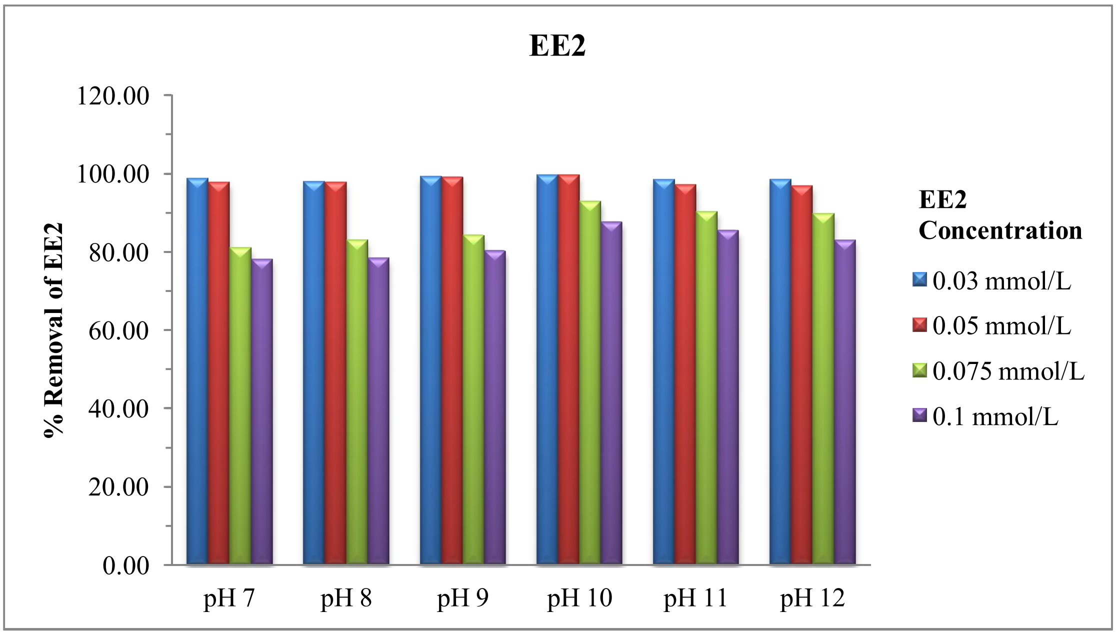


Figure 3.24 Percent removal of 17α-ethynylestradiol (EE2) at different 17α-ethynylestradiol(EE2) concentration and pH. [Fe(VI) dose : 0.1 mmol/L)

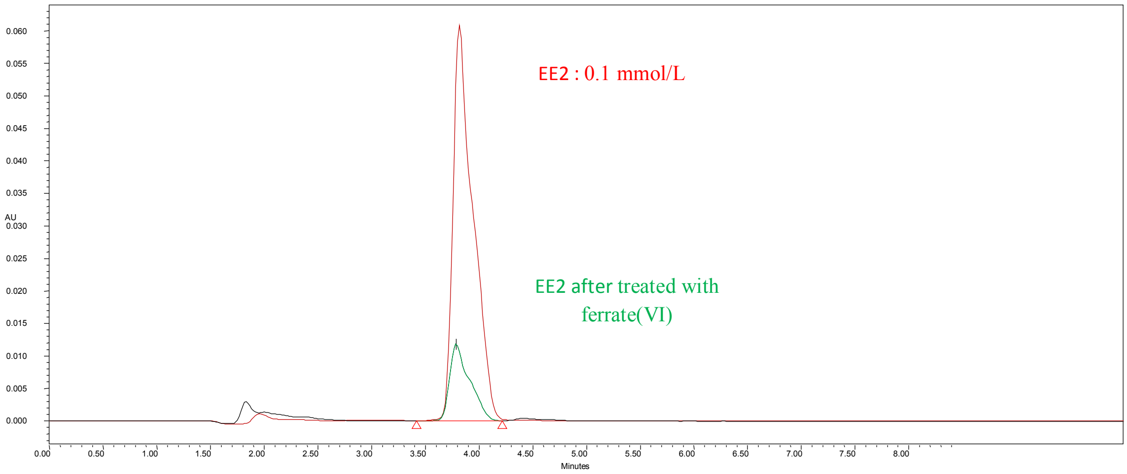


Figure 3.25 Degradation of 17α-ethynylestradiol (EE2) at Fe(VI) : 17α-ethynylestradiol (EE2) molar ratio 1:1 (pH 7).

3.3.3. Effect of pH in the degradation of 17α-ethynylestradiol (EE2) with ferrate(VI)

The pH dependence study is an important parameter which enables to optimize the selectivity of solution pH to degrade the 17α-ethynylestradiol (EE2) from aqueous solution. Moreover, it provides the mechanism involved in the degradation of EE2 with ferrate(VI). The degradation of 17α-ethynylestradiol (EE2) was studied using the HPLC measurements and the results are returned in figure 3.24 as percent removal of 17α-ethynylestradiol (EE2) against the pH and concentration of 17α-ethynylestradiol (EE2). It was observed in general that increasing the concentration of 17α-ethynylestradiol (EE2) was caused to decrease the percent removal of 17α-ethynylestradiol (EE2) at a constant dose of ferrate(VI). More quantitatively, increasing the concentration of 17α-ethynylestradiol (EE2) from 0.03 to 0.1 mmol/L the corresponding decrease in percent removal of 17α-ethynylestradiol (EE2) was found to be from 98.73% to 78.13%, respectively at pH 7.0 at a constant dose of ferrate(VI) 0.10 mmol/L. This decrease in percent removal was due to the fact that at lower concentration of 17α-ethynylestradiol (EE2) relatively more number of ferrate(VI) molecules were present to degrade the lesser number of 17α-ethynylestradiol (EE2) molecules. However, increasing the concentration of 17α-ethynylestradiol(EE2) an apparent increase in content of 17α-ethynylestradiol (EE2) removal was achieved. This indicated that although at lower concentration the percent removal of 17α-ethynylestradiol (EE2) was higher however, the increase in pollutant concentration favored the content removal of pollutant at constant dose of ferrate(VI).

On the other hand the decrease in pH from pH 12.0 to 7.0 does not much affect the percent removal of 17α-ethynylestradiol (EE2) from aqueous solutions (*cf* figure 3.24). Quantitatively, decreasing the pH from 12.0 to 7.0 the corresponding percent degradation of 17α-ethynylestradiol (EE2) was decreased from 82.98% and 78.13%, respectively at the ferrate(VI) to 17α-ethynylestradiol (EE2) molar ratio 1:1. Moreover, it was further observed that at 1:0.3 molar ratio of Fe(VI) : 17α-ethynylestradiol (EE2) and at pH 7.0 to 12.0 the 17αethynylestradiol (EE2) removal was found to be *Ca* 100%; indicated the high reactivity of ferrate(VI) in the removal of EE2 from aqueous solutions..

It was reported that EE2 had pK_a value of 10.4 (Yang *et al.*, 2011). This indicated that EE2 is predominantly present as an neutral molecule up until pH 10.0 and carries a net negative charge above pH 10.4. Because of this, relatively very high adsorptive removal of EE2 by the modified clays was almost unaffected within the pH region 3.0 to 10.0 from aqueous solutions (Thanhmingliana *et al.*, 2015). On the hand, ferrate(VI) possessed with protonated species ($HFeO_4^-$) dominated at pH ~7.0 (Sharma *et al.*, 2001). The reactivity of the protonated species of ferrate(VI) was relatively high, therefore caused an apparent increase in the degradation of EE2 at lower pH values.

3.3.4 Mineralization of 17α-ethynylestradiol (EE2)

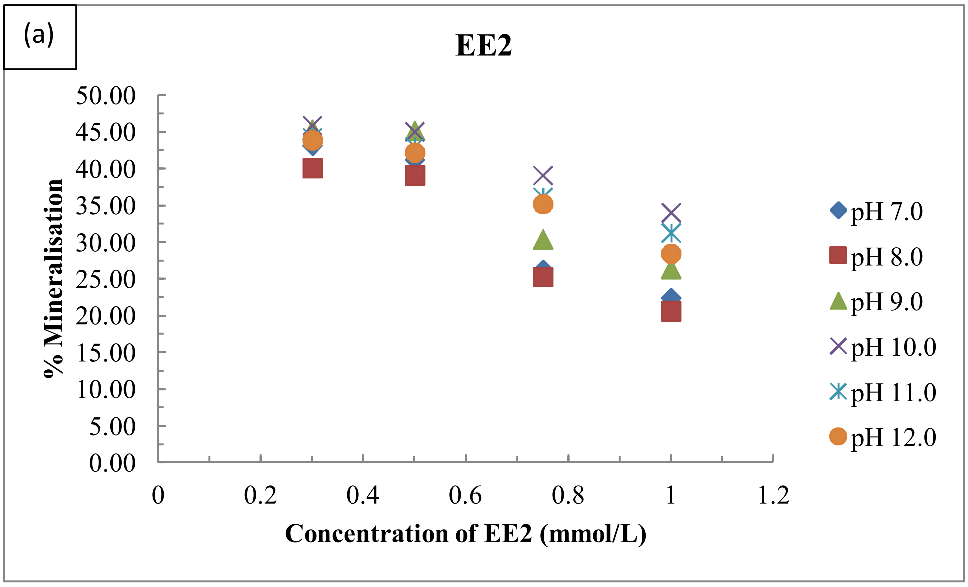
Further, it is interesting to obtain the mineralization of 17α-ethynylestradiol (EE2) with the ferrate(VI) treatment. The samples of 17α-ethynylestradiol (EE2) having varied concentrations (0.03 to 0.1 mmol/L) were treated with a constant dose of ferrate(VI) for a period of 2 hrs at constant but varied pH conditions (pH 7.0 to 12.0) and then the samples were subjected for its bulk TOC (total organic carbon) measurements. The untreated samples of 17α-ethynylestradiol (EE2) were used to measure the initial TOC values. The percent TOC removal were then obtained which is of course an indicative of % mineralization of EE2 from aqueous solutions. The percent TOC removal as a function of pollutant concentration and solution pH was presented graphically in figure 3.26(a). It is evident from the figure 3.26(a) that the decrease in 17α-ethynylestradiol (EE2) concentration and pH greatly favoured the percent removal of TOC. Quantitatively, decreasing the 17α-ethynylestradiol (EE2) concentration from 0.1 to 0.03 mmol/L caused to increase the TOC removal from 22.42 to 43.15% as observed at pH 7.0. Similarly, decreasing the solution pH from 12.0 to 7.0 the corresponding increase in percent TOC removal was found to be 28.46 to 22.42% at the 1:1

molar ratio of the ferrate(VI) to 17α-ethynylestradiol (EE2). The trend of this result is in a line to the kinetic and HPLC results obtained previously. It is also evident from the TOC data that although a partial mineralization of 17α-ethynylestradiol (EE2) was obtained but a significant percent was mineralized with a single dose of ferrate(VI).

On the other hand, the TOC data is further presented in terms of total amount of the 17α-ethynylestradiol (EE2) mineralized by the ferrate(VI) treatment and is presented as function of 17α-ethynylestradiol (EE2) initial concentration and solution pH (*cf* figure 3.26(b)) . It is interesting to observe that increasing the concentration of 17α-ethynylestradiol (EE2) favored significantly the content removal of 17α-ethynylestradiol (EE2) from aqueous solutions.

Table 3.13 Mineralization of 17α-ethynylestradiol (EE2) by ferrate(VI) at different pH and 17α-ethynylestradiol (EE2) concentrations ([Fe(VI)]: 0.1 mmol/L).

pH	**% Mineralisation of EE2 by ferrate(VI)**			
	[Fe(VI)] : [EE2]			
	1:0.3	**1:0.5**	**1:0.75**	**1:1**
7.0	43.15	41.27	26.27	22.42
8.0	40.11	39.12	25.29	20.64
9.0	45.32	45.14	30.42	26.39
10.0	45.87	45.07	39.13	34.02
11.0	44.28	43.06	36.17	31.31
12.0	43.89	42.22	35.22	28.46



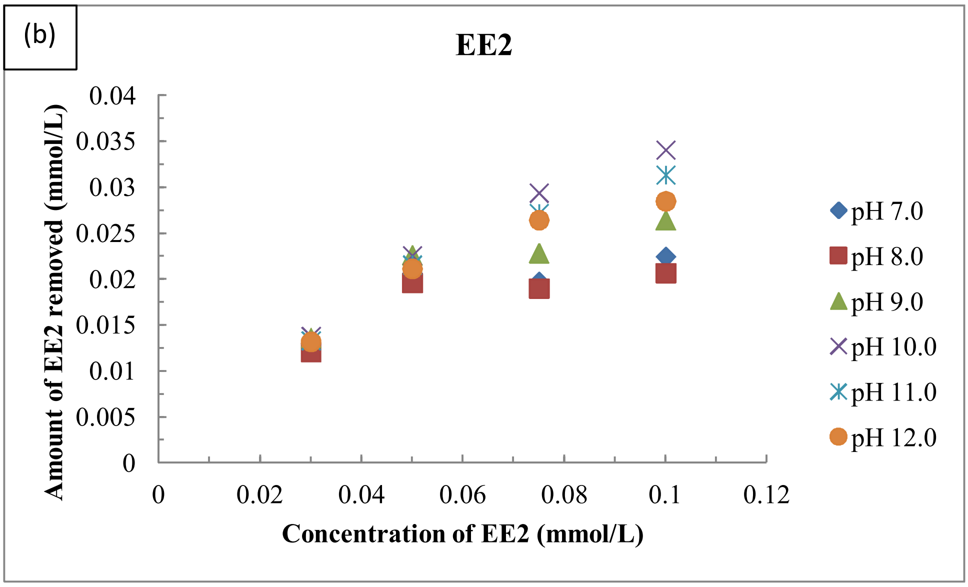


Figure 3.26 (a) Percent mineralisation; and (b) extent removal of 17α-ethynylestradiol (EE2) as a function of pH and 17α-ethynylestradiol (EE2) concentrations at constant dose of ferrate(VI) : 0.1 mmol/L.

3.3.5. Effect of background electrolytes

The presence of co-exiting ions in the removal of 17α-ethynylestradiol (EE2) (0.1 mmol/L) is studied using the ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3 were used as co-existing ions. Variety of electrolytes is used having partly or fully oxidized ions. The results are returned in graphically in figure 3.27 for 17α-ethynylestradiol (EE2). Results indicated that the presence of fully oxidized electrolytes *viz.*, NaCl, $NaNO_3$ and Na_2HPO_4 could not affect significantly the oxidation of 17α-ethynylestradiol (EE2) by ferrate(VI). It is to be noted that presence of phosphate and nitrate also caused to increase slightly the degradation of the 17α-ethynylestradiol (EE2). This is due to the fact that ferrate(VI) is relatively stable in the phosphate media forming complexes with Fe(III) otherwise forming precipitates of iron oxide and which accelerates the spontaneous fast decomposition of ferrate(VI) (Thompson *et al.*, 1951). However, on the other hand the partly oxidized $NaNO_2$ and Na_2SO_3 are caused significantly the decrease in the decomposition of 17α-ethynylestradiol (EE2) from aqueous solutions. The results inferred that the presence of NO_2^- and SO_3^{2-} affected the degradation of 17α-ethynylestradiol (EE2) up to some extent by the ferrate(VI). Previously, it was reported that the presence of NO_2^- and SO_3^- greatly affected the degradation of the Zn(II)-NTA complex by the ferrate(VI) since the ferrate(VI) decomposition was increased significantly in presence of these electrolytes (Yang *et al.*, 2010). Further, the extent of oxidation of 17α-ethynylestradiol (EE2) by the ferrate(VI) was studied increasing the $NaNO_2$ or Na_2SO_3 concentration from 0.1 to 5.0 mmol/L at the constant 17α-ethynylestradiol (EE2) and ferrate(VI) concentration of 1.0 mmol/L and at pH 8.0. The results were returned graphically in figure 3.31. It was noted that increasing the background concentration from 0.1 to 5.0 mmol/L $NaNO_2$ the corresponding decrease in percent removal of 17α-ethynylestradiol (EE2) was from 72.87% to 65.67 % (i.e., 7.2% only), respectively. It is also to be noted that increasing the background concentration from 0.1 to 5.0 mmol/L Na_2SO_3 the corresponding decrease in percent removal of 17α-ethynylestradiol (EE2) is from 69.53% to 60.4% (i.e., 9.13% only), respectively. The insignificant decrease in percent removal of 17α-ethynylestradiol (EE2) even with increasing the partially oxidized electrolytes *viz.*, $NaNO_2$ and Na_2SO_3 pointed the affinity and potential application of ferrate(VI), at least, in the degradation of 17α-ethynylestradiol (EE2) from aqueous solutions.

The TOC data was also obtained in order to estimate the percent mineralization of EE2 by ferrate(VI) in presence of various background electrolytes at pH 8.0 and ferrate(VI) to EE2 molar ratio 1:1. The results were returned graphically in figure 3.27 and in Table 3.14. A partial mineralization was not significantly affected in presence of studied electrolytes. Similarly, the presence of partially oxidized electrolytes viz., $NaNO_2$ and Na_2SO_3 also was not affected significantly the mineralization of EE2 by ferrate(VI) (Figure 3.28).

Table 3.14 Percent removal of 17α-ethynylestradiol (EE2) by ferrate(VI) as a function of different background electrolytes at pH 8.0. (HPLC measurement) (Blank = 78.45% removal)

Electrolyte	**Area(µV*sec)**		**% Removal**
	EE2	**EE2 + electrolyte + Ferrate(VI)**	
Na_2HPO_4	923685	201732	78.16
Na_2SO_4	923685	193327	79.07
$NaNO_3$	923685	201178	78.22
NaCl	923685	204688	77.84
$NaNO_2$	923685	250595	72.87
Na_2SO_3	923685	281446	69.53

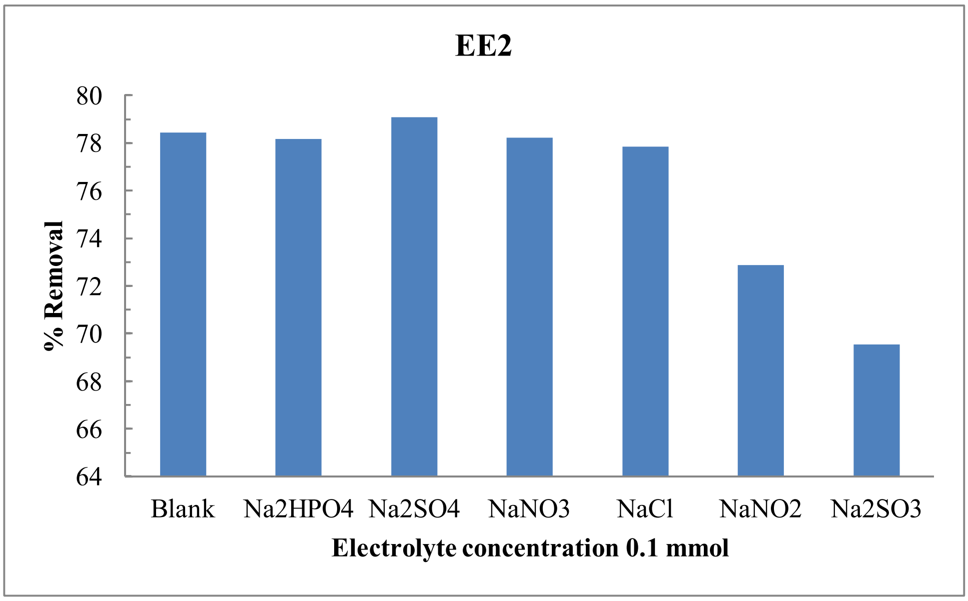


Figure 3.27 Effect of electrolytes in the degradation of 17α-ethynylestradiol (EE2) by ferrate(VI) at pH 8.0.

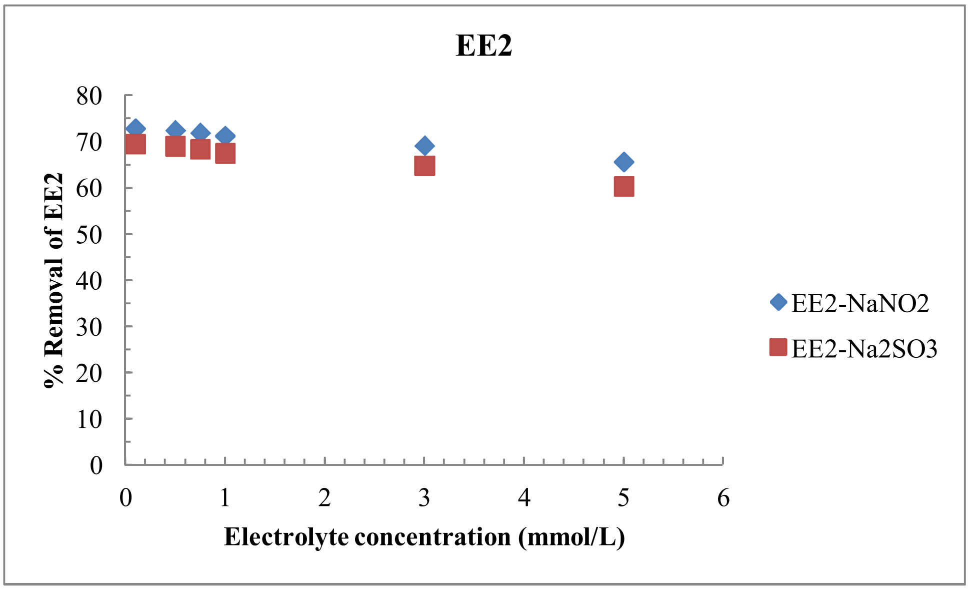


Figure 3.28 Effect of various concentrations of electrolyte in the degradations of 17α-ethynylestradiol (EE2) by ferrate(VI).

Table 3.15 Percent mineralisation of 17α-ethynylestradiol (EE2) by ferrate(VI) as a function of different background electrolytes at pH 8.0. (TOC measurement) (Blank=20.26% mineralization)

Electrolyte	Total Organic Carbon (mg/L)		% Mineralisation
	EE2	EE2 + Electrolyte + Ferrate	
Na_2HPO_4	23.89	18.93	20.76
Na_2SO_4	23.89	18.95	20.68
$NaNO_3$	23.89	18.97	20.59
NaCl	23.89	18.9	20.89
$NaNO_2$	23.89	19.72	17.46
Na_2SO_3	23.89	20.14	15.70

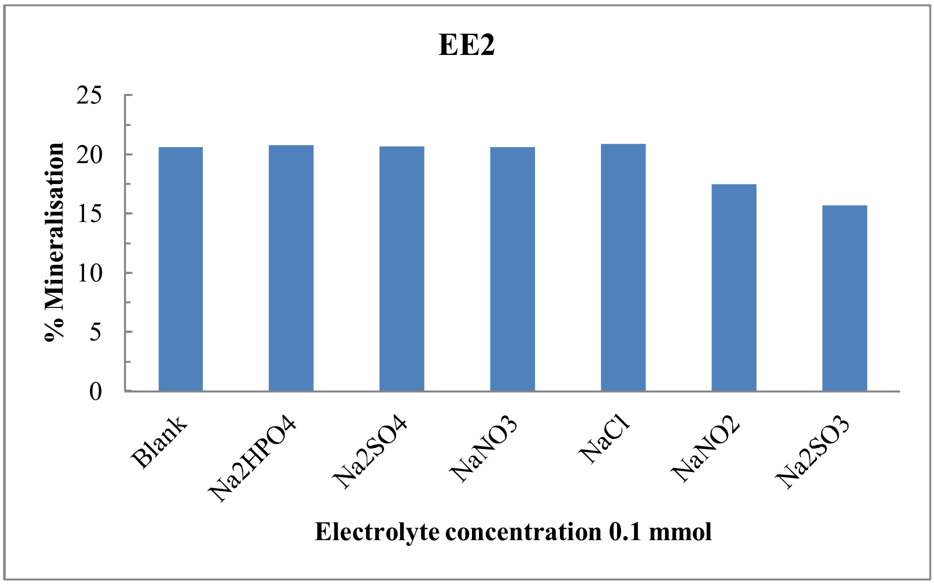


Figure 3.29 Effect of electrolytes in the mineralisation of 17α-ethynylestradiol(EE2) by ferrate(VI) at pH 8.0.

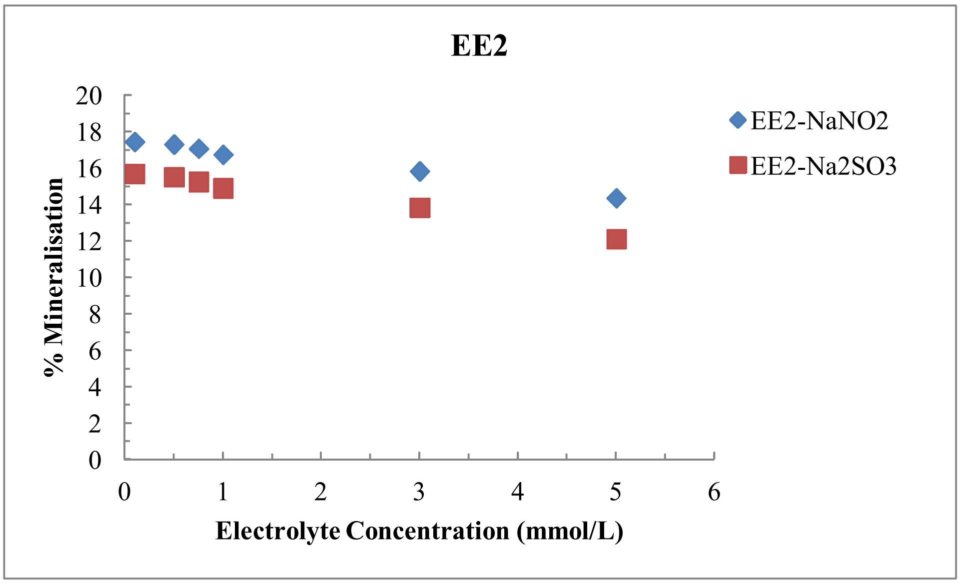


Figure 3.30 Effect of various concentrations of electrolytes $NaNO_2$ and Na_2SO_3 in the mineralisation of 17α-ethynylestradiol (EE2) by ferrate(VI).

3.4. 4-tert-octylphenol

3.4.1. Degradation of 4-tert-octylphenol using UV-Vis measurements

3.4.1.1. Effect of concentration of 4-tert-octylphenol

Another important EDC i.e., 4-tert-octylphenol is also included in the oxidative removal using ferrate(VI) at different pH conditions (i.e., pH 7.0 to 12.0). The pollutant concentration was varied from 0.03 to 0.5 mmol/L and it was treated with a constant ferrate dose of 0.1 mmol/L. In other words the molar ratio of 4-tert-octylphenol to ferrate(VI) was varied from 0.3:1 to 5:1. The results are presented graphically in figure 3.34 for the 4-tert-octylphenol (at pH 8.0 is taken as representative graph). It is evident from the figure that increasing the concentration of 4-tert-octylphenol the reduction of ferrate(VI) was increased sharply. Therefore, it concluded that the degradation of 4-tert-octylphenol was increased significantly with the increase of pollutant concentration at a constant dose of ferrate(VI). Further, it was observed that the ferrate(VI) concentration was decreased sharply during the initial period of contact followed by an apparent equilibrium or the constant concentration of ferrate(VI) was obtained. The maximum decrease of ferrate(VI) concentration was observed within initial *Ca* 5 minutes of contact in presence of this pollutant. This shows that ferrate(VI) is an efficient oxidant, in particular, the degradation of 4-tert-octylphenol from aqueous solutions. Quantitatively, increasing the contact time from 0 to 20 min the amount of ferrate(VI) was decreased from 0.10 to 0.022 mmol/L, respectively in the 1:1 molar ratios of ferrate(VI) and 4-tert-octylphenol.

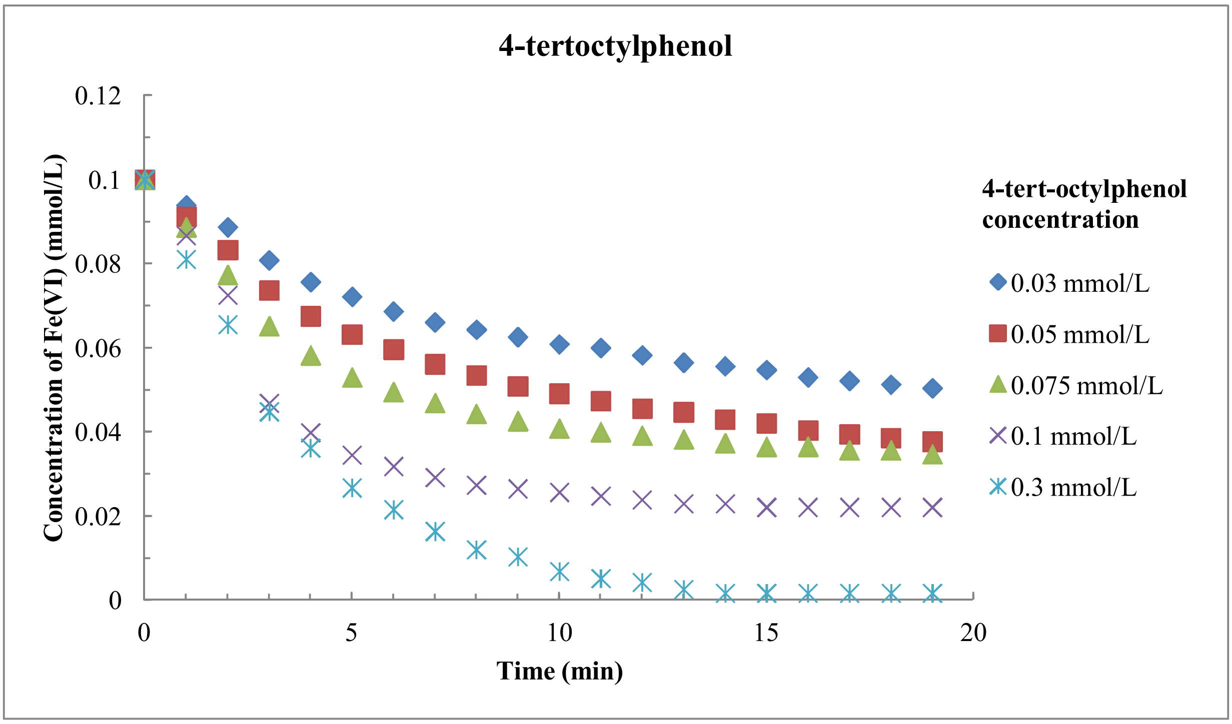


Figure 3.31 Degradation of 4-tert-octylphenol as a function of time at different concentrations of 4-tert-octylphenol at a constant ferrate(VI) dose of 0.1 mmol/L and at constant pH 8.0.

3.4.1.2. Kinetics of ferrate(VI) degradation

Further, the kinetics of the degradation of 4-tert-octylphenol was using the time dependence data obtained for the reduction of ferrate(VI) at neutral pH 7.0. The basic expression could be written in the degradation of 4-tert-octylphenol by ferrate(VI) as :

$$\mathrm{Fe(VI)} + \mathrm{EE2} \rightarrow \mathrm{Fe(III)} + \text{Oxidized Products} + \mathrm{CO_2} \qquad \ldots(3.16)$$

Therefore, the rate of ferrate(VI) reduction in presence of 4-tert-octylphenol could be written as :

$$-\frac{d[Fe(VI)]}{dt} = \mathrm{kapp}\ [Fe(VI)]^m\ [4-tert-octylpheno\ l]^n \qquad \ldots(3.17)$$

where k_{app} is the apparent rate constant of the reduction of ferarte(VI) in presence of 4-tert-octylphenol. Further, at varied concentration of the 4-tert-octylphenol, the above equation could be reduced to :

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)]^m \qquad \ldots(3.18)$$

where, $k = k_{app}\ [4\text{-}tert\text{-}octylphenol]^n$ ...(3.19)

Using the time dependence change in ferrate(VI) concentration data was utilized to fit into the pseudo-first-order rate and pseudo-second-order rate equations as to optimize the value of ‘m’ i.e., either 1 or 2. It was observed that the kinetic data was reasonably fitted well to the pseudo-second order rate kinetics than the pseudo-first order rate kinetics since the R^2 values were found to be high for the pseudo-second order rate law (Table 3.16). This indicated that the value of ‘m’ was 2 with respect to each concentration of 4-tert-octyl phenol and ferrate(VI). It is clearly observed that increasing the 4-tert-octylphenol concentration (from 0.03 to 0.5 mmol/L) greatly favored the degradation of pollutant by ferrate(VI) since the rate constant values were significantly increased with the increase in pollutant concentration. This is due to the fairly high oxidizing capacity of ferrate(VI) towards the pollutants which enables more and more oxidation of the pollutant species in aqueous solutions (García- Araya *et al.*, 2010). It was previously reported that the kinetics of the oxidation of selected carbohydrates and sucralose by ferrate(VI) were followed the pseudo-first-order rate law with respect to each reactant and the rate constant was increased increasing the concentration of carbohydrates or sucralose. Further, the observed second-order rate constants values (k_{app}) were increased with a decrease in pH for disaccharides (Sharma *et al.*, 2012).

Table 3.16 Pseudo second order rate constants estimated in the degradation of ferrate(VI) in presence of 4-tert-octylphenol at pH 7.0.

Ferrate(VI) concentration (mmol/L)	**4-tert-octylphenol concentration (mmol/L)**	**Pseudo-second order rate constant k (L/mol/min)**	**R^2**
0.1	0.03	547.68	0.9727
0.1	0.05	1165	0.9924
0.1	0.075	2071.5	0.9945
0.1	0.1	5354.2	0.9801

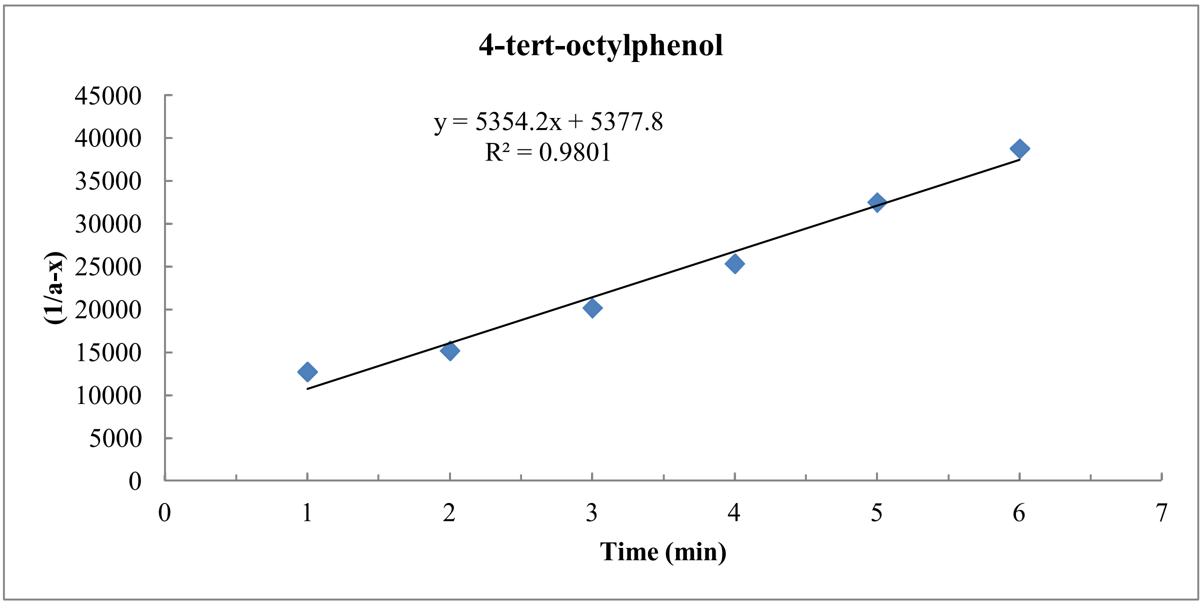


Figure 3.32 Pseudo second order rate kinetics for ferrate(VI) in presence of 4-tert-octylphenol at pH 7.0 (Concentration of Fe(VI) : 0.1 mmol/L, Concentration of 4-tert-octylphenol : 0.1 mmol/L)

Further, the value of 'n' along with the apparent rate constant value k_{app} was estimated using the pseudo-second rate constant values obtained at various concentrations of 4-tert-octylphenol at pH 7.0. The plots were drawn between the concentrations of 4-tert-octylphenol against the estimated 'k' values and returned in figure 3.32. It is clearly demonstrated that the data is reasonably fitted well and hence the value of 'n' is found to be 1. Therefore, the stoichiometric ratio of the ferrate(VI) and 4-tert-octylphenol was found to be 2:1. Moreover, the overall rate constant k_{app} was estimated to be 6605.6 L/mol/min at pH 7.0. Previously, it was reported the degradation of E2, EE2 and bisphenol A was followed the second order rate law and the rate constant values were ranged from the $6.4\text{x}10^2$ to $7.7\text{x}10^2$ L/mol/s at pH 7.0 (Lee *et al*., 2005). The other study indicated that the rate constants for the oxidation of organosulfur compounds by ferrate(VI) at pH 8.0 were calculated and the k_{app} values were vared from $3.1\text{x}10^0$ to $1.8\text{x}10^5$ M^{-1} s^{-1} in which cysteine possessed the highest reactivity and dimethyl sulfoxide (DMSO) reacted sluggishly with ferrate(VI). Among aliphatic thiols, thiourea (TU) and thioacetamide (TA) were the most reactive. Moreover, the aromatic thiols had $k_{app} = 3.8\text{x}10^2–7.2\text{x}10^3$ M^{-1} s^{-1} and the mercaptans showed very high reactivity (k_{app} = $6.0\text{x}10^4$ - $4.0\text{x}10^5$ M^{-1} s^{-1}) (Sharma *et al*., 2011).

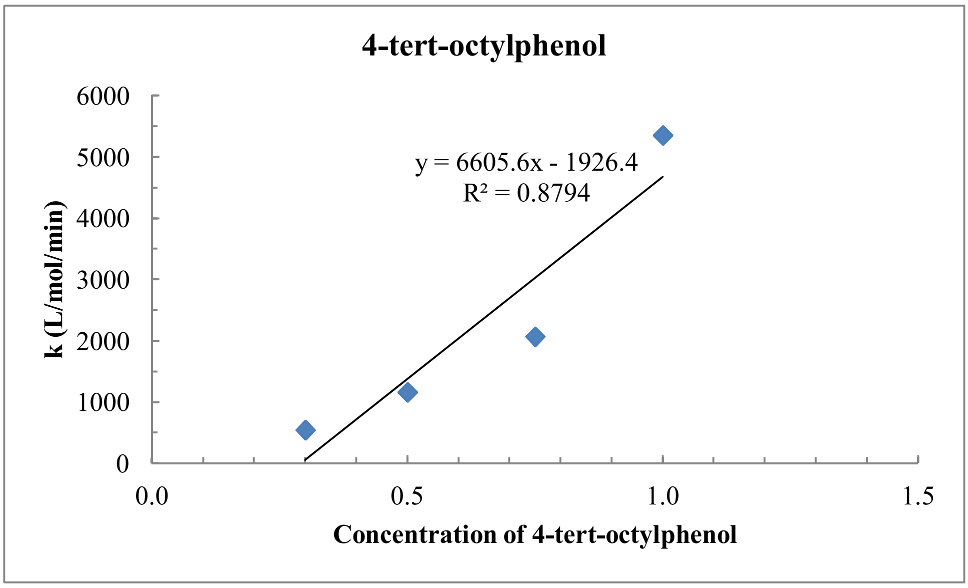


Figure 3.33 Variation of pseudo-second-order rate constants (k) values as a function of 4-tert-octylphenol concentration at pH 7.0.

3.4.2. Removal of 4-tert-octylphenol using HPLC measurements

Further, the removal of 4-tert-octylphenol using ferrate(VI) was determined using the high performance liquid chromatograph (HPLC) equipped with UV detector (Waters 2489 UV/Vis detector). A C18 column (5 μm particle size, 250 mm length, and 4.6 mm inner diameter) was employed with the mobile phase of acetonitrile : water (70:30, v/v). The flow rate of mobile phase was maintained to 1.0 mL/min. An injection volume of 20 μL was used and the concentration of 4-tert-octylphenol was determined using UV detector at 222 nm. A standard blank run of 4-tert-octylphenol showed that the retention time of 4-tert-octylphenol was occurred at 12.19 minutes. The HPLC chromatogram, i.e. peak area was calculated using the EMPOWER2 Software in μV*sec unit which corresponds to the concentration of 4-tert-octylphenol in an aqueous solution. The concentration of 4-tert-octylphenol was varied from 0.03 mmol/L to 0.3 mmol/L whereas the concentration of ferrate(VI) was kept constant at 0.1 mmol/L. The samples were treated separately at pH 7.0 to 12.0 in the batch reactors. The blank 4-tert-octylphenol peak area along with the ferrate(VI) treated 4-tert-octylphenol peak area were utilized to obtain the percent removal of pollutant at all the concentrations of pollutants and at specified pH values. The results were returned in the Table 3.17 and in Figure 3.34. It was found that 98.04% of 4-tert-octylphenol was removed at the 0.03 mmol/L of 4-tert-octylphenol treated at pH 7.0. The removal of 4-tert-octylphenol was decreased as the concentration of 4-tert-octylphenol was increased. High percent removal of 4-tert-octylphenol was obtained at pH 7 because the reactivity of ferrate(VI) was enhanced at lower pH values. The percent removal of 4-tert-octylphenol was decreased as the pH of the solution was increased from pH 7.0 to 12.0. At pH 7.0 and at the Fe(VI) : 4-tert-octylphenol molar ratio 1:1, the percent removal was achieved to 83.84% and the overlay peaks of 4-tert-octylphenol and 4-tert-octylphenol treated with ferrate(VI) was shown in the Figure 3.35.

Table 3.17 Percent Removal of 4-tert-octylphenol species by Fe(VI) at different pH and molar ratio values.

pH	Initial concentration (mmol/L)		Area (µV*sec)	% Removal
	Ferrate(VI)	4-tert-octyl phenol		
7.0	0	0.03	642445	98.04
	0.1	0.03	12578	
	0	0.05	1071357	96.02
	0.1	0.05	42658	
	0	0.075	1607036	93.79
	0.1	0.075	99845	
	0	0.1	2146515	83.84
	0.1	0.1	346789	
	0	0.3	6454347	64.00
	0.1	0.3	2323564	
8.0	0	0.03	639345	96.45
	0.1	0.03	22696	
	0	0.05	1067892	94.67
	0.1	0.05	56918	
	0	0.075	1701245	90.72
	0.1	0.075	157875	
	0	0.1	2167834	81.24
	0.1	0.1	406685	
	0	0.3	6425432	69.89
	0.1	0.3	1934697	
9.0	0	0.03	642237	85.46
	0.1	0.03	93381	
	0	0.05	1101456	79.78
	0.1	0.05	222714	
	0	0.075	1706783	75.07
	0.1	0.075	425501	
	0	0.1	2132583	66.15
	0.1	0.1	721879	
	0	0.3	6434782	47.53
	0.1	0.3	3376330	

Table 3.17 Percent Removal of 4-tert-octylphenol species by Fe(VI) at different pH and molar ratio values

pH	Initial concentration (mmol/L)		Area (µV*sec)	% Removal
	Ferrate(VI)	4-tert-octyl phenol		
10.0	0	0.03	641008	81.62
	0.1	0.03	117817	
	0	0.05	1086145	75.31
	0.1	0.05	268169	
	0	0.075	1603562	69.17
	0.1	0.075	494378	
	0	0.1	2167362	63.56
	0.1	0.1	789786	
	0	0.3	6459054	37.64
	0.1	0.3	4027866	
11.0	0	0.03	641568	76.34
	0.1	0.03	151794	
	0	0.05	1065267	73.04
	0.1	0.05	287195	
	0	0.075	1615879	65.12
	0.1	0.075	563618	
	0	0.1	2135198	58.35
	0.1	0.1	889309	
	0	0.3	6431276	34.78
	0.1	0.3	4194478	
12.0	0	0.03	636587	37.16
	0.1	0.03	400017	
	0	0.05	1072132	34.82
	0.1	0.05	698815	
	0	0.075	1612745	31.03
	0.1	0.075	1112371	
	0	0.1	1916784	25.47
	0.1	0.1	1428579	
	0	0.3	6431687	20.11
	0.1	0.3	5138275	

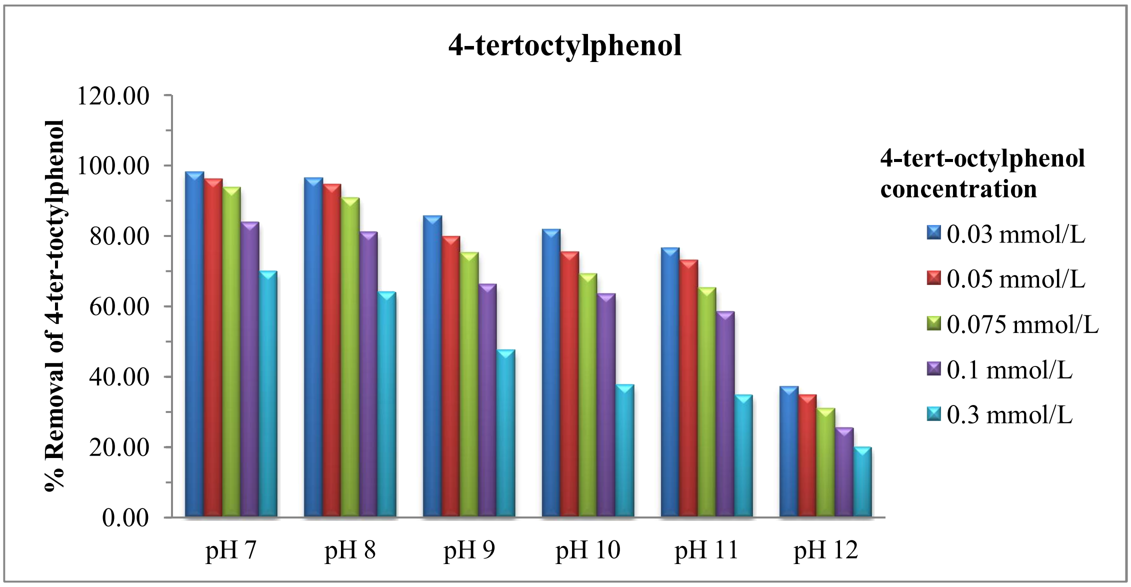


Figure 3.34 Percent removal of 4-tert-octylphenol at different 4-tert-octylphenol concentration and pH. [Fe(VI) dose : 0.1 mmol/L]

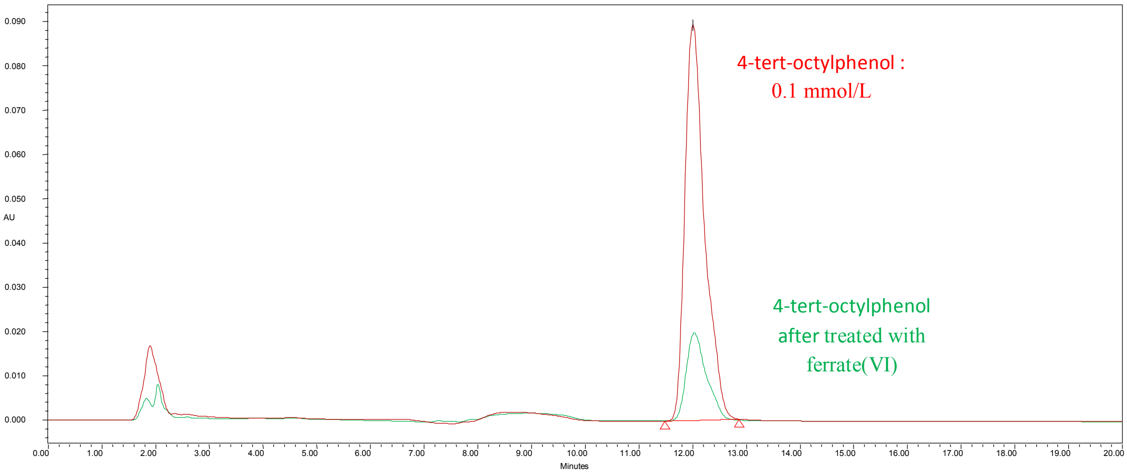


Figure 3.35 Degradation of 4-tert-octylphenol at Fe(VI) : 4-tert-octylphenol molar ratio 1:1 (pH 7.0).

3.4.3. Effect of pH in the degradation of 4-tert-octylphenol with ferrate(VI)

The pH dependence study is then obtained to deduce a plausible mechanism involved in the degradation of 4-tert-octylphenol from aqueous solutions using the ferrate(VI). The HPLC data obtained at different concentrations of 4-tert-octylphenol and at varied pH conditions (pH 7.0 to 12.0) were obtained and returned in Figure 3.34. It was observed that that increasing the concentration of 4-tert-octylphenol apparently caused to decrease the percent removal of 4-tert-octylphenol at a constant dose of ferrate(VI). More quantitatively, increasing the concentration of 4-tert-octylphenol from 0.03 to 0.3 mmol/L the corresponding decrease in percent removal of 4-tert-octylphenol was found to be from 98.04 to 69.89%, respectively at pH 7.0 at a ferrate(VI) dose of 0.10 mmol/L. This decrease in percent removal was due to the fact that at lower concentration of 4-tert-octylphenol relatively more number of ferrate(VI) molecules were present to degrade the lesser number of 4-tert-octylphenol molecules. However, increasing the concentration of 4-tert-octylphenol an apparent increase in content of 4-tert-octylphenol removal was obtained. This indicated that although at lower concentration the percent removal of 4-tert-octylphenol was relatively high, however, the increase in pollutant concentration favoured greatly the content of pollutant removal at constant dose of ferrate(VI).

On the other hand the decrease in pH from pH 12.0 to 7.0 enabled to increase significantly the percent removal of 4-tert-octylphenol from aqueous solutions (*cf* figure 3.34). Quantitatively, decreasing the pH from 12.0 to 7.0 the corresponding percent degradation of 4-tert-octylphenol was increased from 25.47% to 83.84% at the ferrate(VI) to 4-tert-octylphenol molar ratio 1:1. The 4-tert-octylphenol is a weak acid and the pk_a of this compound is *Ca* 10. Therefore, 4-tert-octylphenol is widely distributed in aqueous solution in its un-dissociated form even up until the pH 10.0. However, further increase in pH beyond pH 10.0 it turned into the dissociated anionic form. On the other hand at lower pH values the protonated species of the ferrate(VI) i.e., $HFeO_4^-$ as dominated at lower pH values since the

pK_a value for the acid dissociation of $HFeO_4^-$ was reported to be 7.3 (Sharma *et al.*, 2001) and showed greater reactivity towards variety of water pollutants (Ohta *et al.*, 2001; Sharma *et al.*, 2004). This in fact caused for higher removal of 4-tert-octylphenol from aqueous solutions at lower pH values. It was reported previously that advanced oxidation process using the $UV/TiO_2/S_2O_8^{2-}$ was efficient in the degradation of 4-tert-octylphenol from aqueous solution. The addition of $S_2O_8^{2-}$ greatly improved the degradation rate preventing the recombination process of the photogenerated holes and electrons and by producing SO_4^- radicals that are capable of oxidizing 4-tert-octylphenol (Yamazaki *et al.*, 2008).

It is further noted that at 1:0.3 and 1:0.05 molar ratios of Fe(VI) : 4-tert-octylphenol at pH 7.0, the 4-tert-octyl phenol was almost completely removed indicated the strong reactivity of ferrate(VI) towards the 4-octyl phenol from aqueous solutions.

3.4.4. Mineralization of 4-tert-octylphenol

Further, the mineralization of 4-tert-octylphenol with the ferrate(VI) treatment was obtained using the TOC measurements. The samples of 4-tert-octylphenol having varied concentrations (0.03 to 0.3 mmol/L) were treated with a constant dose of ferrate(VI) for a period of 2 hrs at constant but varied pH conditions (pH 7.0 to 12.0) and then the samples were subjected for its bulk TOC measurements. The untreated samples of 4-tert-octylphenol are also used to measure the initial TOC values of the samples. The percent TOC removal of the 4-tert-octylphenol as a function of pollutant concentration and solution pH was calculated and presented graphically in figure 3.36(a). It is evident from the figure 3.36(a) that the decrease in 4-tert-octylphenol concentration and pH favoured greatly the percent removal of TOC. Quantitatively, decreasing the 4-tert-octylphenol concentration from 0.3 to 0.03 mmol/L was caused to increase the TOC removal from 27.03% to 75.99% as observed at pH 7.0. Similarly, decreasing the solution pH from 12.0 to 7.0 the corresponding increase in percent TOC removal was found to be 13.99% to 30.54% at the 1:1 molar ratio of the ferrate(VI) to 4-tert-octylphenol. Relatively high percent removal of 4-tert-octylphenol is pointed the potential use of ferrate(VI) in the mineralization of this pollutant. Overall, the trend of TOC data is in a line to the HPLC results obtained previously. It is also evident from the TOC data that although a partial mineralization of 4-tert-octylphenol was obtained but a significant percent was mineralized with the single dose of ferrate(VI).

On the other hand the data is further presented in terms of total amount of the 4-tert-octylphenol mineralized by the ferrate(VI) treatment and are presented as a function of 4-tert-octylphenol initial concentration and solution pH (*cf* figure 3.36(b)). It is interesting to observe that increasing the concentration of 4-tert-octylphenol favored significantly the content of 4-tert-octylphenol removal from aqueous solutions. Whereas the decrease in pH (i.e., from pH 12.0 to 7.0) favoured greatly the content removal of 4-tert-octylphenol.

Table 3.18 Percent mineralisation of 4-tert-octylphenol by ferrate(VI) at different pH and 4-tert-octyl-phenol concentrations (ferrate(VI) concentration 0.1 mmol/L)

pH	**% Mineralisation of Total Organic Compound by using Fe(VI)**				
	[Ferrate(VI)] : [4-tert-octylphenol]				
	1:0.3	**1:0.5**	**1:0.75**	**1:1**	**1:3**
7.0	75.99	57.62	48.81	30.54	27.03
8.0	71.62	55.16	46.87	28.00	25.01
9.0	65.83	51.21	41.75	24.63	21.14
10.0	63.71	41.99	38.65	22.20	17.27
11.0	59.24	41.04	36.66	18.32	15.19
12.0	36.84	25.92	20.59	13.99	10.27

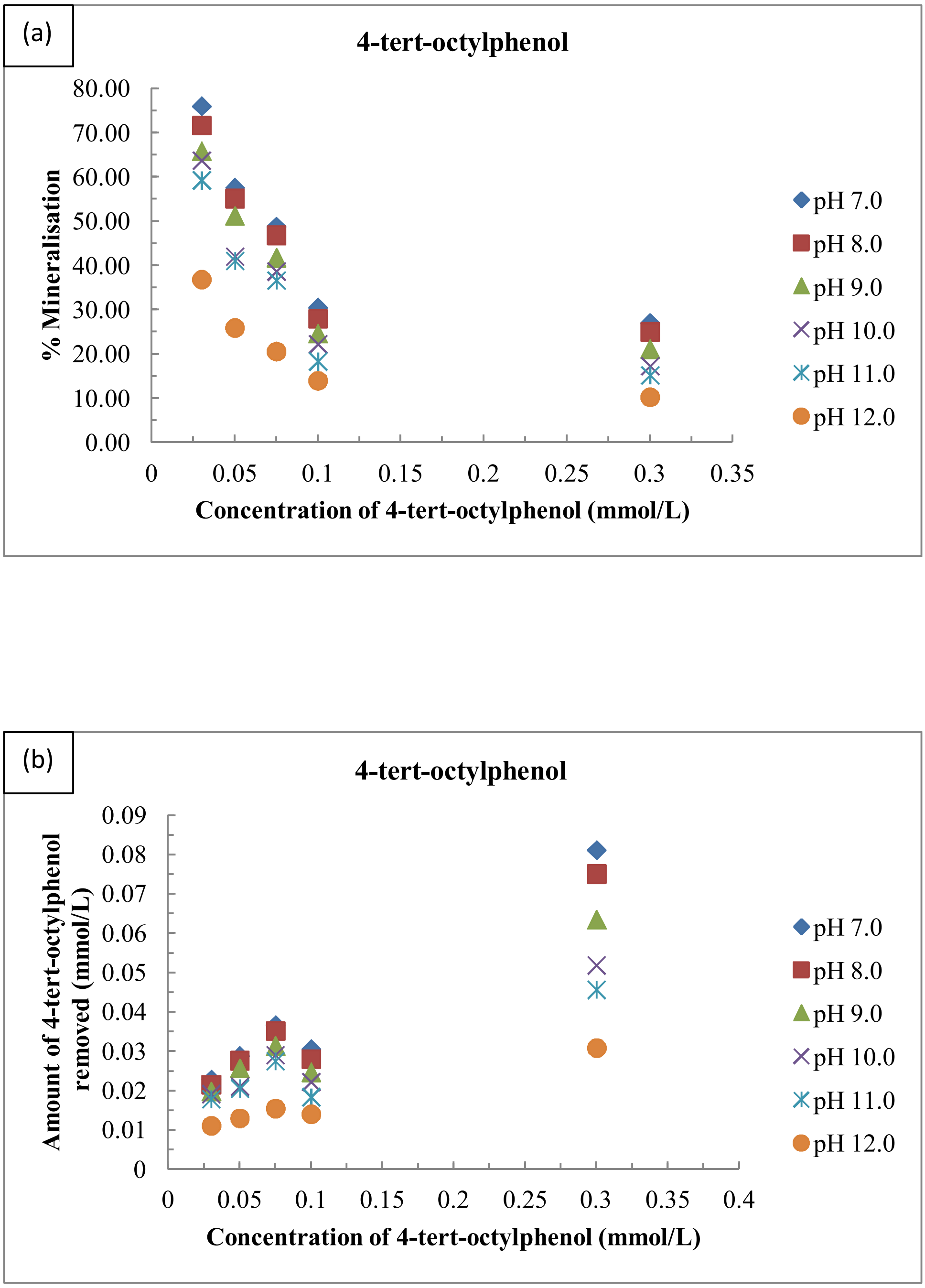


Figure 3.36 (a) Percent removal; and (b) extent removal of 4-tert-octylphenol as a function of pH and 4-tert-octylphenol concentrations at a constant dose of ferrate(VI) : 0.1 mmol/L.

3.4.5. Effect of background electrolytes

The presence of co-existing ions in the removal of 4-tert-octylphenol (0.1 mmol/L) was studied using a ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3 were chosen as co-existing ions. Variety of electrolytes is used having partly or fully oxidized ions. The results are returned graphically in figure 3.37 for the degradation of 4-tert-octylphenol using ferrate(VI) as a function of various electrolytes. Results indicated that the presence of fully oxidized electrolytes *viz.*, NaCl, $NaNO_3$ and Na_2HPO_4 could not affect significantly the oxidation of 4-tert-octylphenol by ferrate(VI). However, on the other hand the partly oxidized $NaNO_2$ and Na_2SO_3 electrolytes were caused upto some extent to decrease the decomposition of 4-tert-octylphenol from aqueous solutions. Previously, it was reported that the presence of NO_2^- and SO_3^- greatly affected the degradation of the Zn(II)-NTA complex by the ferrate(VI) since the ferrate(VI) decomposition was increased significantly in presence of these electrolytes (Yang *et al.*, 2010). Further, the extent of oxidation of 4-tert-octylphenol by the ferrate(VI) was studied increasing the $NaNO_2$ or Na_2SO_3 concentration from 0.1 to 5.0 mmol/L at a constant 4-tert-octylphenol and ferrate(VI) concentration of 0.1 mmol/L and at pH 8.0. The results are returned graphically in figure 3.38. It was noted that increasing the background concentration from 0.1 to 5.0 mmol/L $NaNO_2$ the corresponding decrease in percent removal of 4-tert-octylphenol was from 76.45 to 67.23 % (i.e., 9.22% only), respectively. Almost similar decrease was observed in presence of Na_2SO_3 for the 4-tert-octylphenol removal. An insignificant decrease in percent removal of 4-tert-octylphenol even with increasing the partially oxidized electrolytes *viz.*, $NaNO_2$ and Na_2SO_3 pointed the affinity and potential application of ferrate(VI), at least, in the degradation of 4-tert-octylphenol from aqueous solutions.

Table 3.19 Percent removal of 4-tert-octylphenol by ferrate(VI) as a function of different background electrolytes at pH 8.0. (HPLC measurement)

Electrolyte	**Area(µV*sec)**		**% Removal**
	4-tert-octylphenol	**4-tert-octylphenol + Electrolyte + Ferrate**	
Na_2HPO_4	2167834	409287	81.12
Na_2SO_4	2167834	382839	82.34
$NaNO_3$	2167834	409937	81.09
NaCl	2167834	380671	82.44
$NaNO_2$	2167834	510524	76.45
Na_2SO_3	2167834	539357	75.12

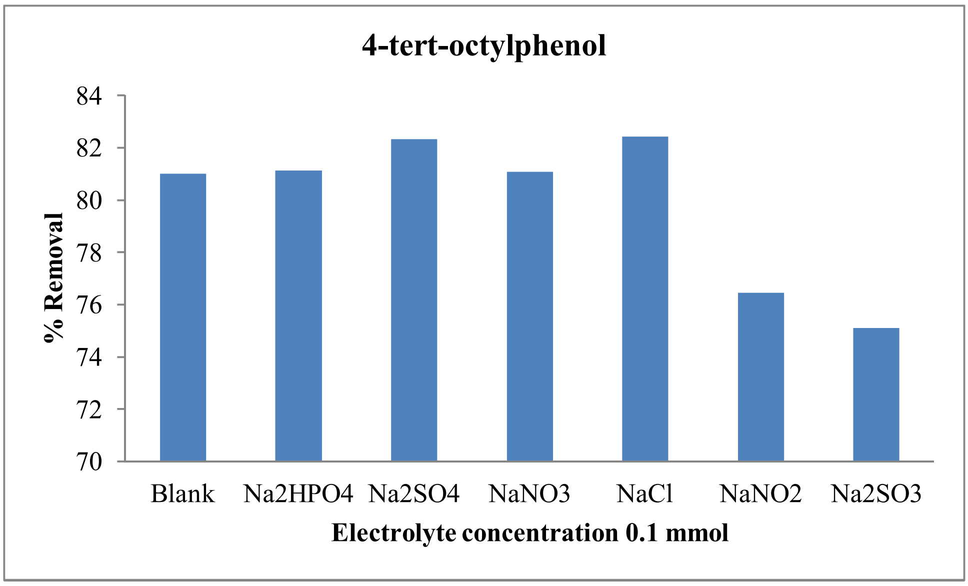


Figure 3.37 Effect of electrolytes in the degradation of 4-tert-octylphenol by ferrate(VI) at pH 8.0.

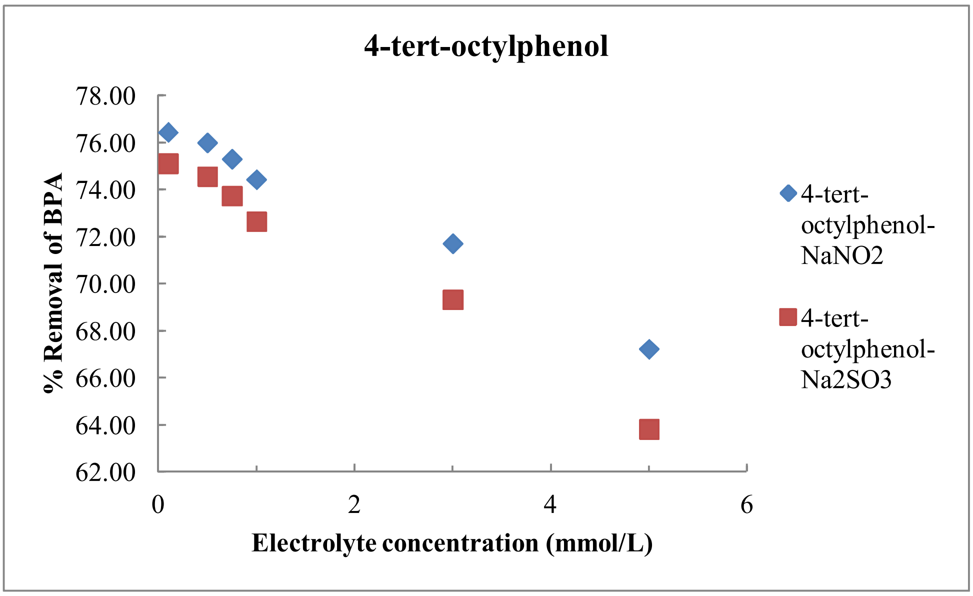


Figure 3.38 Effect of various concentrations of electrolyte in the degradations of 4-tert-octylphenol by ferrate(VI).

Table 3.20 Percent mineralisation of 4-tert-octylphenol by ferrate(VI) as a function of different background electrolytes at pH 8.0. (HPLC measurement)

Electrolyte	**Total Organic Carbon (mg/L)**		**% Mineralisation**
	4-tert-octylphenol	**4-tert-octylphenol + electrolyte + Ferrate**	
Na_2HPO_4	16.75	12.01	28.30
Na_2SO_4	16.75	12.02	28.24
$NaNO_3$	16.75	12	28.36
NaCl	16.75	12.02	28.24
$NaNO_2$	16.75	12.65	24.48
Na_2SO_3	16.75	12.95	22.69

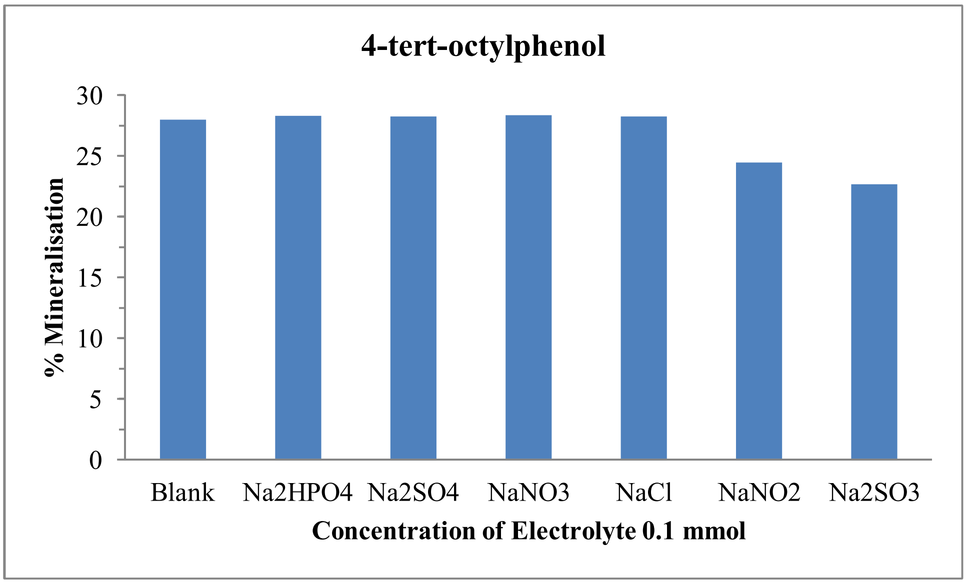


Figure 3.39 Effect of electrolytes in the mineralisation of 4-tert-octylphenol by ferrate(VI) at pH 8.0.

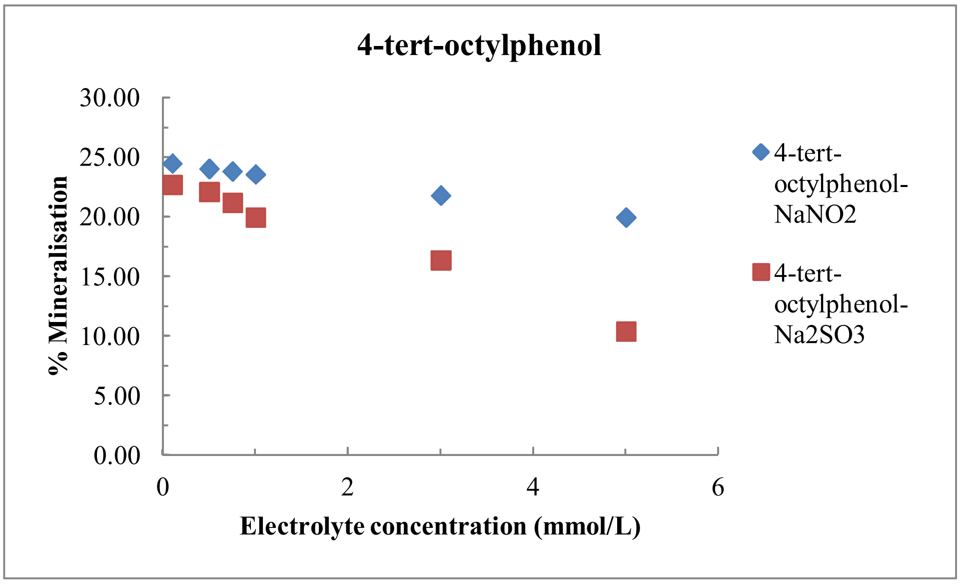


Figure 3.40 Effect of various concentrations of electrolytes $NaNO_2$ and Na_2SO_3 in the mineralisation of 4-tert-octylphenol by ferrate(VI).

3.5. Potassium phthalate

3.5.1. Degradation of Potassium phthalate using UV-Vis measurements

3.5.1.1. Effect of concentration of potassium phthalate

Potassium phthalate was treated at different pH (i.e., pH 7.0 to 12.0) conditions and at varied molar ratios of ferrate(VI) to potassium phthalate (i.e., from 1:0.3 to 1:5). In other words, the potassium phthalate concentration was varied from 0.03 mmol/L to 0.5 mmol/L with a constant ferrate(VI) dose of 0.1 mmol/L. The results were presented graphically in Figure 3.41 for the potassium phthalate (at pH 8.0 was taken as representative graph). It was evident from the figure that increasing the concentration of potassium phthalate the reduction of ferrate(VI) was increased sharply. Therefore, the degradation of the pollutants were increased significantly with the increase of pollutant concentration at a constant dose of ferrate(VI). Further, it was observed that the ferrate(VI) concentration was decreased continuously within time. Quantitatively, increasing the contact time from 0 to 20 min the amount of ferrate(VI) was decreased from 0.10 to 0.089 mmol/L for potassium phthalate in the 1:1 molar ratios of ferrate(VI) and potassium phthalate.

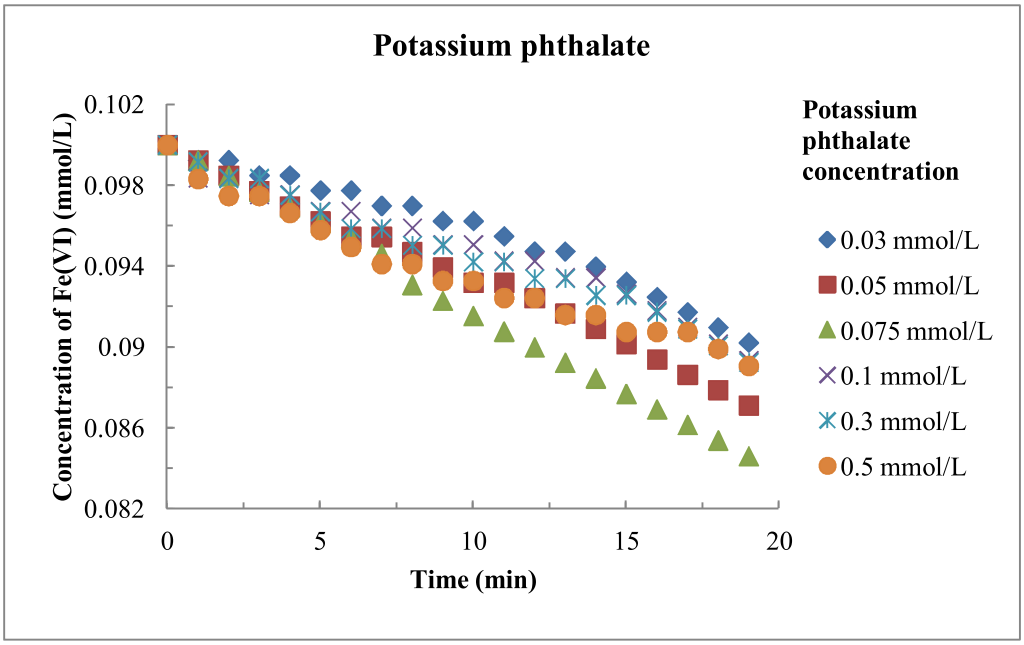


Figure 3.41 Degradation of potassium phthalate as a function of time for diferrent concentration of potassium phthalate for the constant ferrate(VI) dose of 0.1 mmol/L ferrate(VI) at constant pH 8.0.

3.5.1.2. Kinetics of ferrate(VI) degradation

The kinetics of the degradation of potassium phthalate was deduced using the time dependence change in ferrate(VI) concentration at a neutral pH 7.0. The rate expression of ferrate(VI) reduction in presence of potassium phthalate could be written as :

$$-\frac{d[Fe(VI)]}{dt}=k_{\mathrm{app}}\,[Fe(VI)]^{m}\,[Potassium\ \ phthalate\,]^{n} \qquad \ldots(3.20)$$

where k_{app} is an apparent rate constant of the degradation of ferrate(VI) in presence of potassium phthalate. Further, at varied concentrations of the potassium phthalate, the above equation could be reduced to :

$$-\frac{d[Fe(VI)]}{dt}=k[Fe(VI)]^{m} \qquad \ldots(3.21)$$

where, $k = k_{app}$ [Potassium phthalate]^n ...(3.22)

Using the time dependence change in ferrate(VI) concentration was utilized to fit into the pseudo-first-order and pseudo-second-order rate equations as to optimize the value of ‘m’ either 1 or 2. It was observed that the kinetic data was reasonably fitted well to the pseudo-second order rate kinetics comparing to the pseudo-first order rate equations (Table 3.21). This indicated that the value of ‘m’ was 2 with respect to the degradation of ferrate(VI) in presence of potassium phthalate. Therefore, the pseudo-second order rate constant values were estimated and returned in table 3.21 with the regression coefficient (R^2). It is clearly observed that increasing the potassium phthalate concentration (from 0.03 to 0.5 mmol/L) was rendered significantly to increase the pseudo-second order rate constant values for this pollutant. This was due to the fairly high oxidizing capacity of ferrate(VI) towards the pollutants which enabled more and more oxidation of the pollutant species in aqueous solutions (García- Araya *et al.*, 2010).

Table 3.21 Pseudo-second order rate constants estimated in the degradation of ferrate(VI) in presence of potassium phthalate at pH 7.0.

Ferrate(VI) concentration (mmol/L)	**Potassium phthalate concentration (mmol/L)**	**Pseudo-second order rate constant k (L/mol/min)**	**R^2**
0.1	0.03	47.436	0.961
0.1	0.05	51.142	0.944
0.1	0.075	56.099	0.954
0.1	0.1	72.83	0.949
0.1	0.3	84.59	0.976
0.1	0.5	86.822	0.982

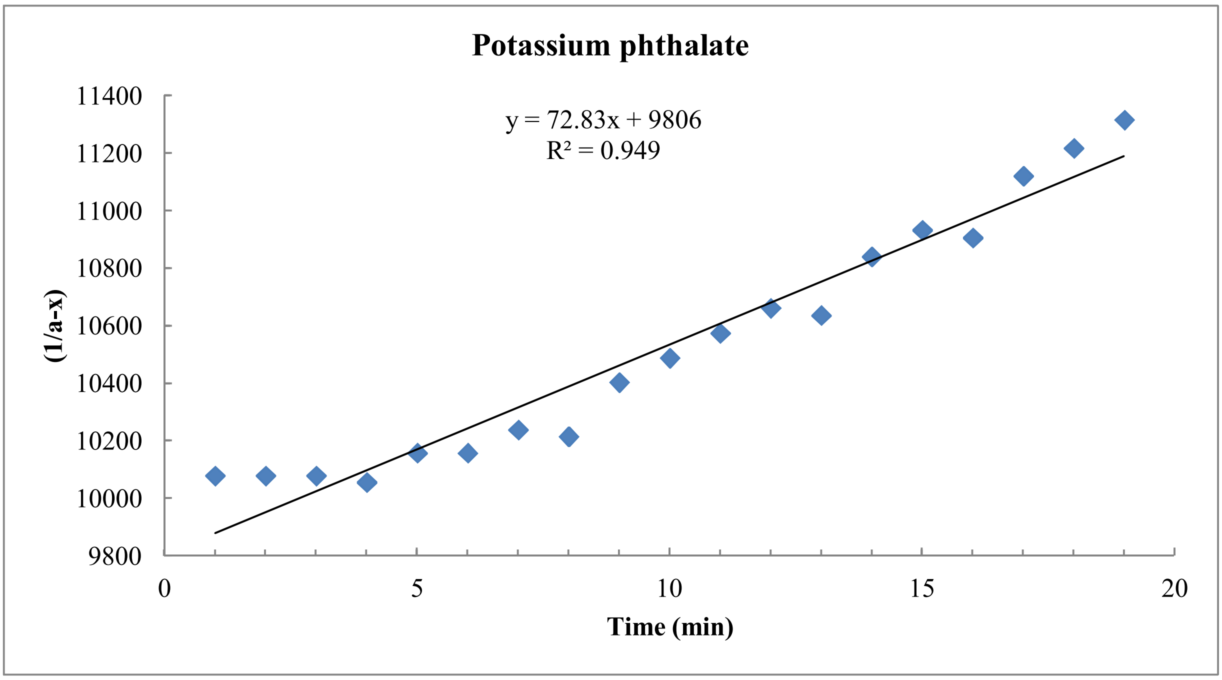


Figure 3.42 Pseudo second order rate kinetics for ferrate(VI) in presence of potassium phthalate at pH 7.0 (Concentration of Fe(VI) : 0.1 mmol/L, Concentration of potassium phthalate : 0.1 mmol/L).

Further, the value of ‘n’ along with the apparent rate constant value k_{app} was estimated using the pseudo-second rate constant values obtained at varied concentrations of potassium phthalate at pH 7.0. The plots were drawn between the concentrations of potassium phthalate against the estimated ‘k’ values and returned in figure 3.43. It was clearly demonstrated that the data was not reasonably fitted well even the value of ‘n’ was taken to be 1. The stoichiometric ratio of the ferrate(VI) and potassium phthalate was expected to be 2:1. Moreover, the overall rate constant k_{app} was estimated and found to be 8.1347 L/mol/min. Previously, it was reported that the degradation of E2, EE2 and bisphenol A was followed the second order rate law and the rate constant values were ranged from the 6.4×10^2 to 7.7×10^2 L/mol/s at pH 7.0 (Lee *et al*., 2005).

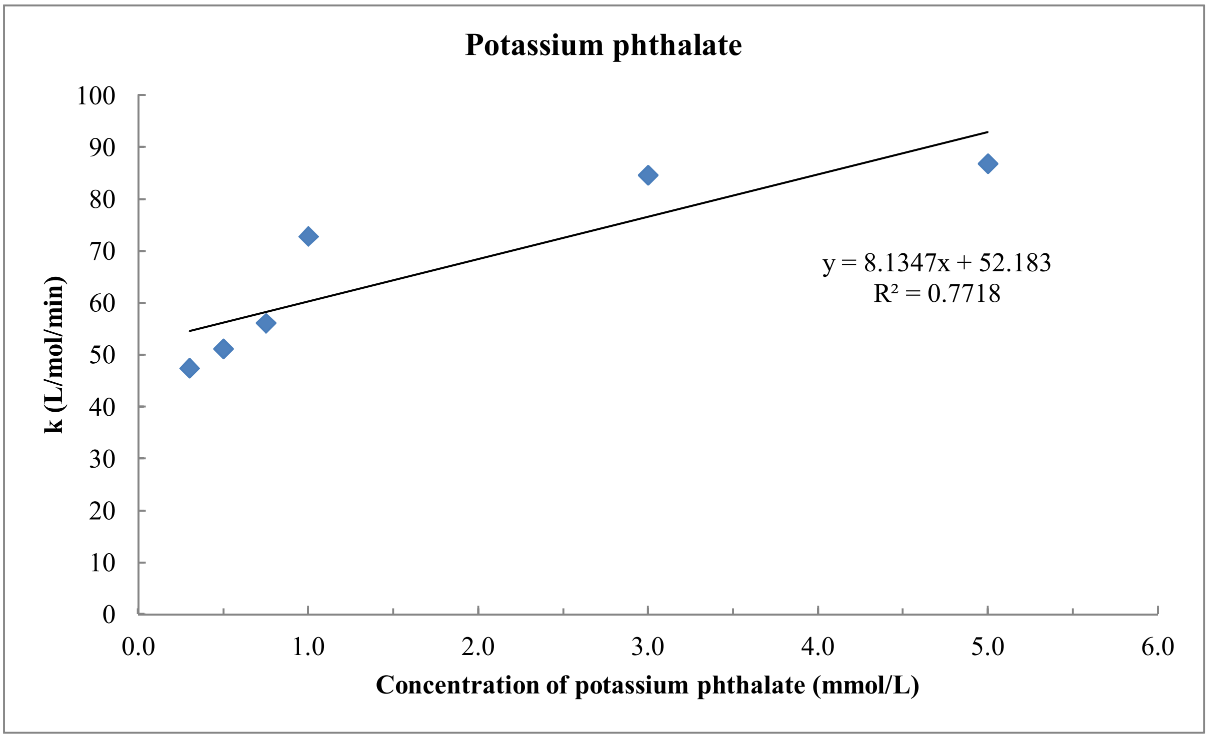


Figure 3.43 Variation of pseudo-second order rate constants (k) values as a function of potassium phthalate at pH 7.0.

3.5.2. Removal of potassium phthalate species using HPLC measurements

The potassium phthalate concentration was determined by using an instrument known as high performance liquid chromatography (HPLC), with a high pressure pump (Waters 515 HPLC pump), a UV detector (Waters 2489 UV/Vis detector). In the HPLC analysis, a C18 column (5 µm particle size, 250 mm length, and 4.6 mm inner diameter) at 25ºC was employed and a mobile phase of acetonitrile : water (70:30, v/v) was used at a flow rate of 1 mL/min. An injection volume of 20 µl was used and the concentration of potassium phthalate was determined by the UV detector at 230 nm. Before analysing the samples, the standard calibration curve of potassium phthalate was run and the chromatogram was appeared at the retention time of 1.78 minute. The HPLC chromatogram, i.e. peak area was calculated by using EMPOWER2 software in µV*sec unit which corresponds to the concentration of potassium phthalate in an aqueous solution. The concentration of potassium phthalate was varied from 0.03 mmol/L to 0.5 mmol/L whereas the concentration of ferrate(VI) was kept constant at 0.1 mmol/L. So, the Fe(VI) : potassium phthalate molar ratio was 1:0.3, 1:0.5, 1:0.75, 1:1, and 1:3. And all these different molar concentrations were studied separately at pH 7.0 to 12.0. The potassium phthalate peak area and the potassium phthalate treated with ferrate(VI) was compared and the percent removal was calculated. It was found that 76.13% of potassium phthalate was removed in the 0.1 mmol/L of ferrate(VI) and 0.03 mmol/L of potassium phthalate at pH 7.0 as shown in the table 3.22. The removal of potassium phthalate was decreased as the concentration of potassium phthalate was increased. High percent removal of potassium phthalate was obtained at pH 7.0 because the reactivity of ferrate(VI) was enhanced at lower pH. The percent removal was decreased as the pH of the aqueous solution increase from pH 7.0 to 12.0. At pH 7.0, in the ferrate(VI) : potassium phthalate molar concentration 1:1, the percent removal was 51.16% and the overlay peaks of potassium phthalate and potassium phthalate treated with ferrate(VI) was shown in the figure 3.45.

Table 3.22 Percent removal of potassium phthalate species by ferrate(VI) at different pH and molar ratio values.

pH	Initial concentration (mmol/L)		Area (µV*sec)	% Removal
	Ferrate(VI)	Potassium phthalate		
7.0	0	0.03	831030	76.13
	0.1	0.03	198366	
	0	0.05	1385050	65.17
	0.1	0.05	482412	
	0	0.075	2077576	59.04
	0.1	0.075	850975	
	0	0.1	2770101	51.16
	0.1	0.1	1352917	
	0	0.3	8310304	30.07
	0.1	0.3	5811395	
	0	0.5	13850506	16.03
	0.1	0.5	11630269	
8.0	0	0.03	831253	70.13
	0.1	0.03	248295	
	0	0.05	1384561	59.04
	0.1	0.05	567116	
	0	0.075	2112376	54.18
	0.1	0.075	967890	
	0	0.1	2780324	46.04
	0.1	0.1	1500262	
	0	0.3	8320674	24.16
	0.1	0.3	6310399	
	0	0.5	13763592	14.11
	0.1	0.5	11821549	
9.0	0	0.03	832497	64.23
	0.1	0.03	297784	
	0	0.05	1387645	56.09
	0.1	0.05	609314	
	0	0.075	2109767	51.14
	0.1	0.075	1030832	
	0	0.1	2769045	43.10
	0.1	0.1	1575586	
	0	0.3	8329874	22.23
	0.1	0.3	6478143	
	0	0.5	13765325	11.06
	0.1	0.5	12242880	

Table 3.22 Percent removal of potassium phthalate species by ferrate(VI) at different pH and molar ratio values.

pH	Initial concentration (mmol/L)		Area (µV*sec)	% Removal
	Ferrate(VI)	Potassium phthalate		
10.0	0	0.03	832195	58.13
	0.1	0.03	348440	
	0	0.05	1390348	46.17
	0.1	0.05	748424	
	0	0.075	2065329	40.05
	0.1	0.075	1238164	
	0	0.1	2787941	28.23
	0.1	0.1	2000905	
	0	0.3	8311873	20.15
	0.1	0.3	6637030	
	0	0.5	137634803	9.04
	0.1	0.5	125192616	
11.0	0	0.03	831254	42.18
	0.1	0.03	480631	
	0	0.05	1380583	33.24
	0.1	0.05	921677	
	0	0.075	2064307	29.05
	0.1	0.075	1464625	
	0	0.1	2784365	16.23
	0.1	0.1	2332462	
	0	0.3	8318765	11.16
	0.1	0.3	7390390	
	0	0.5	13865309	6.41
	0.1	0.5	12976542	
12.0	0	0.03	821346	40.12
	0.1	0.03	491821	
	0	0.05	1347892	31.34
	0.1	0.05	925462	
	0	0.075	2098791	26.19
	0.1	0.075	1549117	
	0	0.1	2770982	14.35
	0.1	0.1	2373346	
	0	0.3	8390583	8.32
	0.1	0.3	7692486	
	0	0.5	13876493	4.53
	0.1	0.5	13247887	

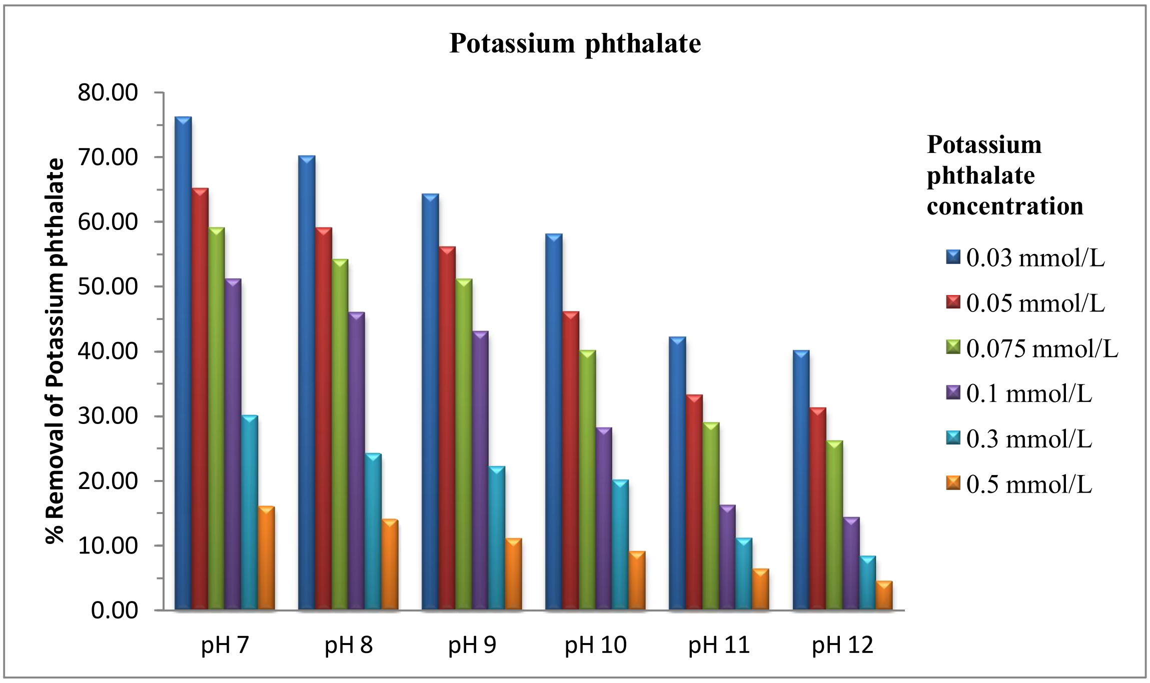


Figure 3.44 Percent removal of potassium phthalate at different potassium phthalate concentration and pH. [Fe(VI) dose : 0.1 mmol/L)

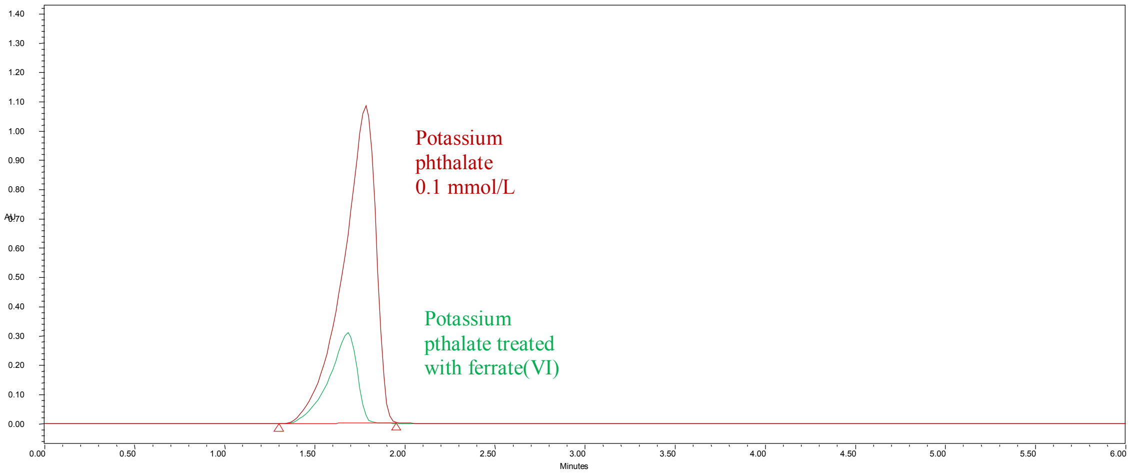


Figure 3.45 Degradation of potassium phthalate at Fe(VI) : potassium phthalate molar ratio 1:1 (pH 7).

3.5.3. Effect of pH in the degradation of potassium phthalate with ferrate(VI)

The pH dependence study was conducted in the degradation of potassium phthalate using ferrate(VI) at varied pH values of treatment i.e., pH 7.0 and 12.0. This provides the mechanism involved in the degradation of pollutants with ferrate(VI). The degradation of potassium phthalate was further studied using the HPLC data and the results are returned in figure 3.44 as percent removal of potassium phthalate against the pH and concentration of potassium phthalate. It was observed in general that increasing the concentration of potassium phthalate was caused to decrease in percent removal of potassium phthalate at a constant dose of ferrate(VI). More quantitatively, increasing the concentration of potassium phthalate from 0.03 to 0.5 mmol/L the corresponding decrease in percent removal of potassium phthalate was found to be from 76.13 to 16.03%, respectively at pH 7.0 at ferrate(VI) dose of 0.1 mmol/L. This decrease in percent removal was due to the fact that at lower concentration of potassium phthalate, relatively more number of ferrate(VI) molecules were present to degrade the lesser number of potassium phthalate molecules. However, increasing the concentration of potassium phthalate an apparent increase in content of potassium phthalate removal was achieved. This indicated that although at lower concentration the percent removal of potassium phthalate was higher however, the increase in pollutant concentration favored significantly the content of potassium phthalate removal at constant dose of ferrate(VI).

On the other hand, the decrease in pH from pH 12.0 to 7.0 enabled to increase significantly the percent removal of potassium phthalate from aqueous solutions (*cf* figure 3.44). Quantitatively, decreasing the pH from 12.0 to 7.0 the corresponding percent degradation of potassium phthalate was increased from 14.35% to 51.16% at the ferrate(VI) to potassium phthalate molar ratio 1:1. The speciation studies conducted elsewhere showed that at around pH 7.0 the protonated species of the ferrate(VI) i.e., $HFeO_4^-$ dominated since the pK_a value for the acid dissociation of $HFeO_4^-$ is reported to be 7.3 (Sharma *et al.*, 2001):

$$HFeO_4^- \leftrightarrow FeO_4^{2-} \qquad (pk_a=7.3) \qquad \ldots(3.23)$$

The reactivity of protonated species is significantly increased due to the protonated species possessed larger spin density (Ohta *et al.*, 2001; Sharma *et al.*, 2004). Similarly, the redox potential of ferrate(VI) was gradually increased with the decrease in pH which again enhanced the reactivity of the ferrate(VI) at lower pH conditions. The other studies indicated that the hybrid technique i.e., UV/Fe(VI)/TiO_2 in presence of N_2 atmosphere was found efficient in the degradation of dimethyl phthalate at pH 9.0 (Yuan *et al.*, 2008).

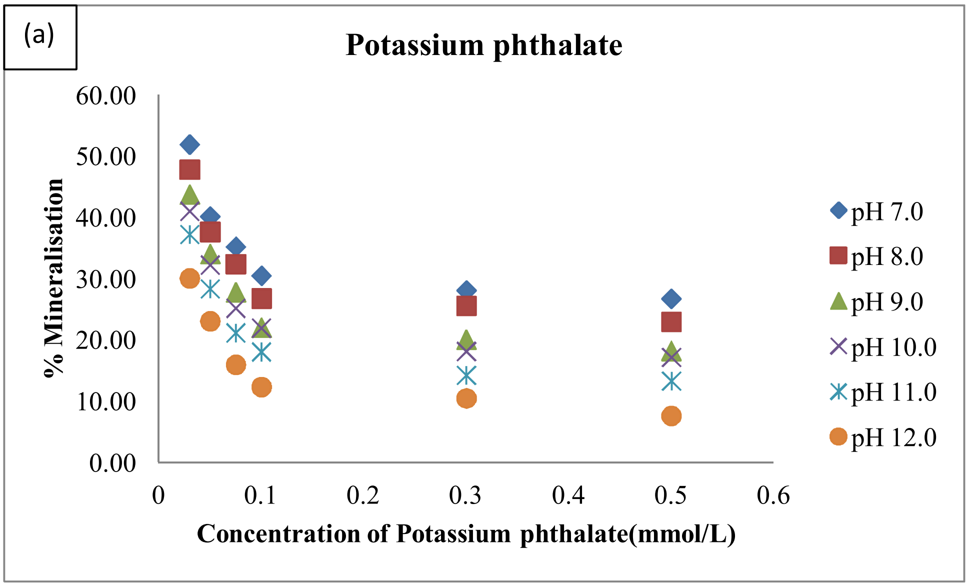
3.5.4. Mineralization of potassium phthalate

Further, it was interesting to obtain the mineralization of the potassium phthalate with the ferrate(VI) treatment. The samples of potassium phthalate having varied concentrations (0.03 to 0.5 mmol/L) were treated with a constant dose of ferrate(VI) for a period of 2 hrs at constant but varied pH conditions (pH 7.0 to 12.0) and then the samples were subjected for the estimation of the TOC (total organic carbon) values. The untreated samples of potassium phthalate were also used to measure the initial TOC values. The percent TOC removal of the potassium phthalate as a function of pollutant concentration and solution pH was calculated and presented graphically in figure 3.46(a). It is evident from the figure 3.46(a) that the decrease in potassium phthalate concentration and pH favoured the percent removal of TOC from aqueous solutions. Quantitatively, decreasing the potassium phthalate concentration from 0.5 to 0.03 mmol/L caused to increase the TOC removal from 16.03% to 76.13% as observed at pH 7.0. Similarly, decreasing the solution pH from 12.0 to 7.0 the corresponding increase in percent TOC removal from 14.35% to 51.16% at the 1:1 molar ratio of the ferrate(VI) to potassium phthalate. The trend of this result is in a line to the HPLC results obtained previously. It is also evident from the TOC data that although a partial mineralization of potassium phthalate was obtained but a significant percent was mineralized with a single dose of ferrate(VI).

On the other hand the data was further presented in terms of total amount of the potassium phthalate mineralized by the ferrate(VI) treatment and were presented as function of potassium phthalate initial concentration and solution pH (*cf* figure 3.46(b)) . It is interesting to observe that increasing the concentration of potassium phthalate favoured significantly the content removal of potassium phthalate from aqueous solutions. Whereas the decrease in pH (i.e., from pH 12.0 to 7.0) favoured the content removal of potassium phthalate.

Table 3.23 Mineralisation of potassium phthalate by ferrate(VI) at different pH and potassium phthalate concentrations (Fe(VI) concentration 0.1 mmol/L)

pH	**% Removal of Total Organic Compound by using Fe(VI)**					
	Fe(VI) : [Potassium phthalate]					
	1:0.3	**1:0.5**	**1:0.75**	**1:1**	**1:3**	**1:5**
7.0	51.96	40.21	35.28	30.53	28.13	26.80
8.0	47.87	37.70	32.45	26.82	25.63	23.02
9.0	43.79	34.12	27.86	22.05	20.12	18.26
10.0	41.10	32.31	25.22	21.98	18.20	17.22
11.0	37.28	28.37	21.23	18.10	14.29	13.32
12.0	30.12	23.12	16.01	12.38	10.53	7.66



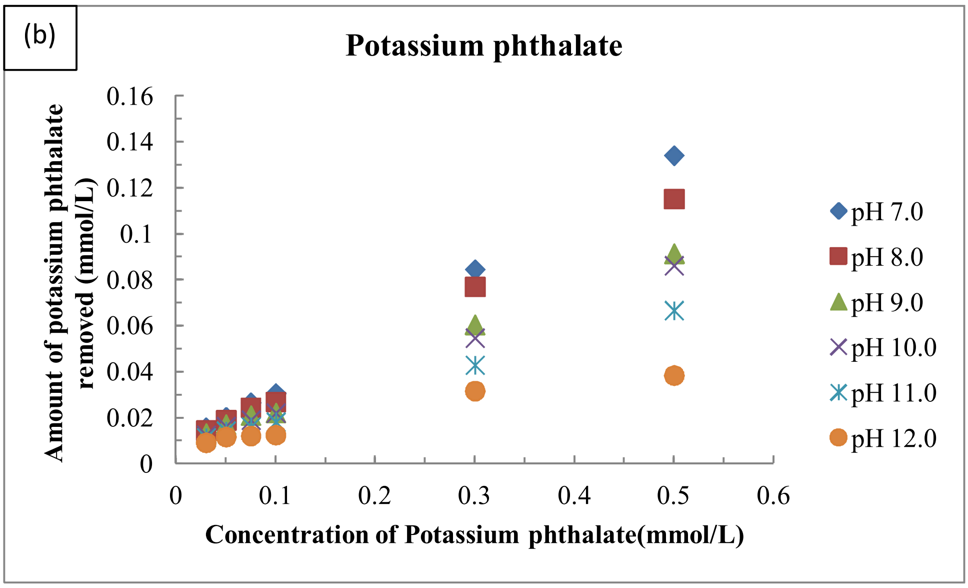


Figure 3.46 (a) Percent removal; and (b) extent removal of potassium phthalate as a function of pH and potassium phthalate concentrations at a constant dose of ferrate(VI) : 0.1 mmol/L.

3.5.5. Effect of background electrolytes

The presence of co-exiting ions in the oxidation of potassium phthalate (0.1 mmol/L) was studied using the ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3 were then used as co-existing ions. The results are returned graphically in figure 3.47. Results indicated that the presence of fully oxidized electrolytes viz., NaCl, $NaNO_3$ and Na_2HPO_4 could not affect significantly the oxidation of potassium phthalate by ferrate(VI). However, on the other hand the partly oxidized $NaNO_2$ and Na_2SO_3 were caused significantly the decrease in the decomposition of potassium phthalate from aqueous solutions. The results inferred that the presence of NO_2^- and SO_3^{2-} affect the degradation of potassium phthalate up to some extent by the ferrate(VI). Previously, it was reported that the presence of NO_2^- and SO_3^- greatly affected the degradation of the Zn(II)-NTA complex by the ferrate(VI) since the ferrate(VI) decomposition was increased significantly in presence of these electrolytes (Yang *et al.*, 2010). Further, the extent of oxidation of potassium phthalate by the ferrate(VI) was studied increasing the $NaNO_2$ or Na_2SO_3 concentration from 0.1 to 5.0 mmol/L at a constant potassium phthalate and ferrate(VI) concentration of 0.1 mmol/L and at pH 8.0. The results are returned graphically in figure 3.48. It is to be noted that increasing the background concentration from 0.1 to 5.0 mmol/L $NaNO_2$ the corresponding decrease in percent removal of potassium phthalate was from 43.02 to 39.96% (i.e., 3.06% only), respectively. Almost similar insignificant decrease in percent decomposition of potassium phthalate was observed in presence of varied concentration of Na_2SO_3 (cf figure 3.49). The insignificant decrease in percent removal of potassium phthalate even with increasing the partially oxidized electrolytes *viz.*, $NaNO_2$ and Na_2SO_3 pointed the affinity and potential application of ferrate(VI), at least, in the degradation of potassium phthalate from aqueous solutions.

Table 3.24 Percent removal of potassium phthalate by ferrate(VI) as a function of different background electrolytes at pH 8.0. (HPLC measurement)

Electrolyte	**Area(µV*sec)**		**% Removal**
	Potassium phthalate	**Potassium phthalate + electrolyte + Ferrate**	
Na_2HPO_4	2780324	1507769	45.77
Na_2SO_4	2780324	1499706	46.06
$NaNO_3$	2780324	1496648	46.17
NaCl	2780324	1503877	45.91
$NaNO_2$	2780324	1584228	43.02
Na_2SO_3	2780324	1586174	42.95

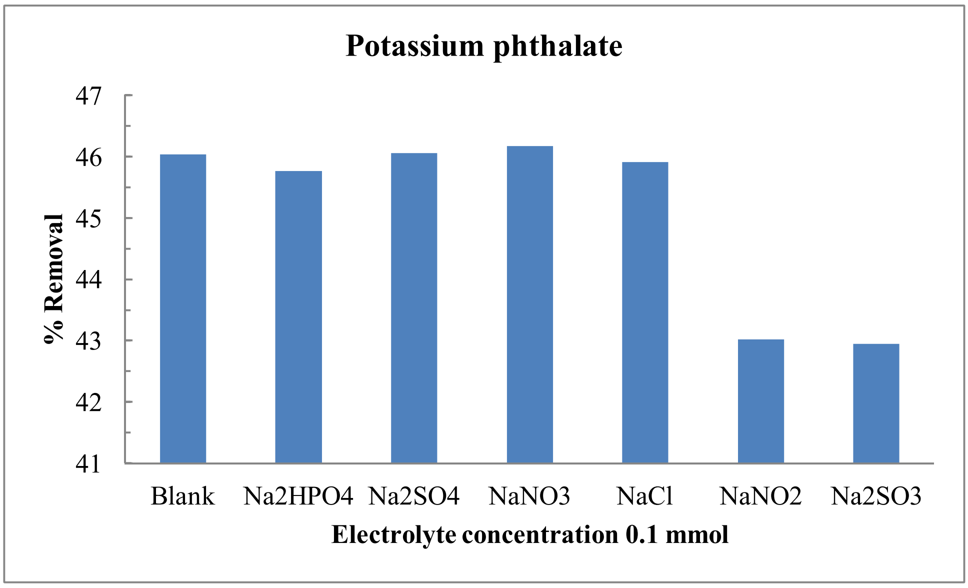


Figure 3.47 Effect of electrolytes in the degradation of potassium phthalate by ferrate(VI) at pH 8.0.

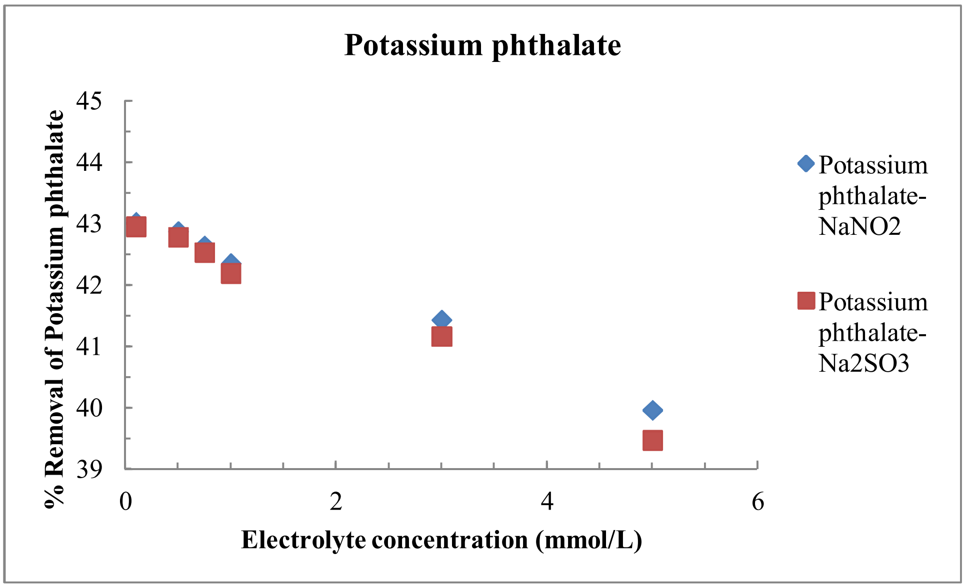


Figure 3.48 Effect of various concentrations of electrolyte in the degradations of potassium phthalate by ferrate(VI).

Table 3.25 Percent mineralisation of potassium phthalate by ferrate(VI) as a function of different background electrolytes at pH 8.0. (TOC measurement)

Electrolyte	**Total Organic Carbon (mg/L)**		**% Mineralisation**
	Potassium phthalate	**Potassium phthalate + electrolyte + Ferrate(VI)**	
Na_2HPO_4	10.7	7.83	26.82
Na_2SO_4	10.7	7.8	27.10
$NaNO_3$	10.7	7.84	26.73
NaCl	10.7	7.85	26.64
$NaNO_2$	10.7	8.34	22.06
Na_2SO_3	10.7	8.55	20.09

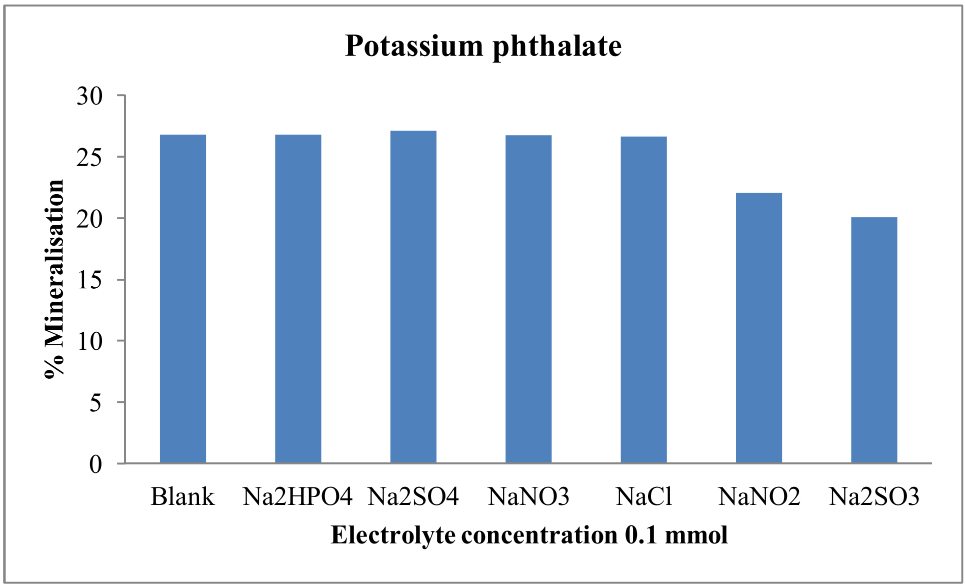


Figure 3.49 Effect of electrolytes in the mineralisation of potassium phthalate by ferrate(VI) at pH 8.0.

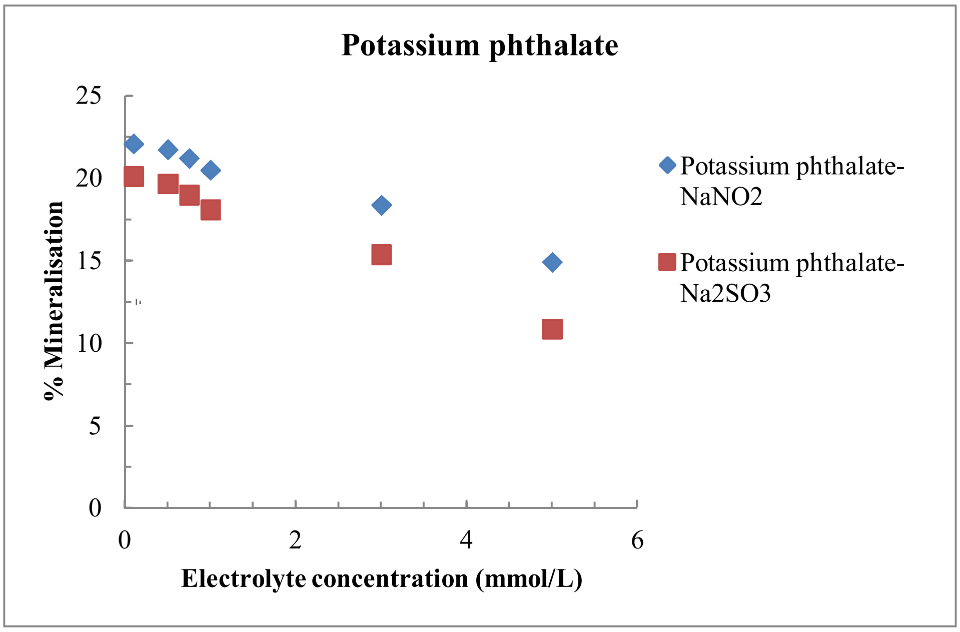


Figure 3.50 Effect of various concentrations of electrolytes $NaNO_2$ and Na_2SO_3 in the mineralisation of potassium phthalate by ferrate(VI).

CHAPTER

4

CONCLUSIONS

4. CONCLUSIONS

Ferrate(VI) in the form of potassium ferrate (K_2FeO_4) was synthesized in the laboratory by wet oxidation method. The purity of the synthesized ferrate(VI) was determined with the help of UV-Visible spectrophotometer at the wavelength of 510 nm and was found to be above 95%. The highly reactive ferrate(VI) was fully employed to assess its efficiency towards the treatment several micro-pollutants in particular the degradation of endocrine disrupting chemicals (EDCs) *viz.*, bisphenol A (BPA), diclofenac sodium salt (DFS), 17α-ethynylestradiol (EE2), 4-tert-octylphenol and potassium phthalate from aqueous solutions. The batch reactor operations were performed for various parametric studies in order to assess the suitability/efficiency of ferrate(VI) along with to deduce a plausible mechanism involved in the oxidative degradation of these EDCs. The EDCs were treated at a wide range of pH i.e., from pH 7.0 to 12.0 and at varied concentration of EDCs from 0.03 mmol/L to 0.5 mmol/L using a constant dose of ferrate(VI) i.e., 0.1 mmol/L. The kinetics of ferrate(VI) reduction was conducted in order to reveal the stoichiometry of EDCs with ferrate(VI). It was observed that a 2:1 molar stoichiometry with ferrate to EDCs was obtained in the oxidative degradation of these EDCs by ferrate(VI). It was further evaluated the k_{app} (overall rate constant) values in the oxidation of EDCs was evaluated and was found to be in the order of bisphenol A > EE2 > 4-tert-octylphenol > diclofenac sodium salt > potassium phthalate at pH 7.0. Generally, it was observed that the reactivity of ferrate(VI) was highly pH dependent towards the degradation of EDCs. It was observed from the UV-Visible analytical data that there was a fast degradation at low pH and the rate of degradation was also increased with the increase in EDCs concentrations. The time dependence data showed that a major extent of EDCs were degraded within just *ca* 10 mins of contact time indicated an extremely high efficiency of ferrate(VI) towards these EDCs.

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

The mineralization of ferrate(VI) treated EDCs samples was obtained with the help of total organic carbon (TOC) analysis. This could apparently enables to estimate the mineralization of these EDCs using a single dose of ferrate(VI). Results showed that a partial but significant amount of the EDCs were mineralized even with the single dose of ferrate(VI). It was found that 45.12% of bisphenol A (BPA), 38.25% of diclofenac sodium salt (DFS), 43.15% of 17α-ethynylestradiol (EE2), 75.99% of 4-tert-octylphenol and 51.96% of potassium phthalate was mineralized for the molar ratio of Fe(VI) : EDCs as 1:0.3 at pH 7.0. Therefore, the degree of TOC percent removal followed the order of 4-tert-octylphenol > potassium phthalate > bisphenol A > 17α-ethynylestradiol (EE2) > diclofenac sodium salt. The decrease in pH of solution greatly favoured the percent mineralization of these pollutants from aqueous solutions. Therefore, pH 7.0 showed relatively higher percent mineralization of all these pollutants. Ferrate(VI) possessesed higher redox potential at acidic conditions and hence accounted for its enhanced reactivity to degrade the organic impurities at lower pH values. The results are explicitly in conformity with the higher redox potential of ferrate(VI) at lower pH values with significant increase in the stability at higher pH values; the redox potential of ferrate(VI) was 2.20 V at pH 1.0 whereas it was only 0.72 V at pH 12.0. Moreover, the protonated ferrate species i.e., $HFeO_4^-$ ($HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-}$; pK_a^2=7.3) which was dominant at lower pH values (pH 7.0) possessed with larger spin density than the deprotonated species *viz*., FeO_4^{2-} caused for increased reactivity of ferrate(VI) at lower pH values.

Further, the effect of ionic strength and background electrolyte concentrations on the removal of these EDCs were studied using the ferrate(VI) dose 0.1 mmol/L at constant initial pH 8.0. The Na_2HPO_4, Na_2SO_4, $NaNO_3$, NaCl, $NaNO_2$ and Na_2SO_3 were used as co-existing ions. Variety of electrolytes is used having partly or fully oxidized ions. Results indicated that the presence of fully oxidized electrolytes viz., NaCl, $NaNO_3$ and Na_2HPO_4 could not affect significantly the oxidation of BPA by ferrate(VI). It is to be noted that presence of phosphate and nitrate also caused to increase slightly the degradation of the EDCs. This is due to the fact that ferrate(VI) is relatively stable in the phosphate media forming complexes with Fe(III) otherwise forming precipitates of iron oxide which accelerates the spontaneous fast decomposition of ferrate(VI). However, on the other hand the partly oxidized $NaNO_2$ and Na_2SO_3 are caused significantly the decrease in the decomposition of EDCs from aqueous solutions. The results inferred that the presence of NO_2^- and SO_3^{2-} affect the degradation of BPA up to some extent by the ferrate(VI). Further, the extent of oxidation of EDCs by the ferrate(VI) was studied increasing the $NaNO_2$ or Na_2SO_3 concentration from 0.1 to 5.0 mmol/L at constant BPA and ferrate(VI) concentrations of 0.1 mmol/L and at pH 8.0. It was noted that increasing the background concentration from 0.1 to 5.0 mmol/L $NaNO_2$ the corresponding decrease in percent removal of bisphenol A (BPA) was from 55.54 to 50.42 % (i.e., 5.12% only), diclofenac sodium salt (DFS) from 39.06% to 35.95 % (i.e., 3.11% only), 17α-ethynylestradiol (EE2) from 72.87% to 65.67 % (i.e., 7.2% only), 4-tert-octylphenol from 76.45 to 67.23 % (i.e., 9.22% only) and potassium phthalate from 43.02 to 39.96 % (i.e., 3.06% only), respectively. Similarly, for the similar increase in Na_2SO_3 background electrolyte concentration from 0.1 to 5.0 mmol/L was caused for insignificant decrease in percent removal of these EDCs from aqueous solutions. Therefore, even in presence of partially oxidized electrolytes *viz*., $NaNO_2$ and Na_2SO_3 the degradation of BPA, DCF, EE2, 4-tert-octylphenol and potassium phthalate was almost unaffected by the ferrate(VI) clearly pointed the affinity and potential application of ferrate(VI), at least, in the degradation of studied EDCs from aqueous solutions.

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

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LIST OF PUBLICATIONS

LIST OF PUBLICATIONS

A. Journals

1. Diwakar Tiwari, **Lalsaimawia Sailo**, Lalramnghaki Pachuau. Remediation of aquatic environment contaminated with the iminodiacetic acid metal complexes using ferrate(VI). *Separation and Purification Technology,* 132 (2014) 77-83.
2. **Lalsaimawia Sailo**, Lalramnghaki Pachuau, Jae Kyu Yang, Seung Mok Lee, Diwakar Tiwari. Efficient use of ferrate(VI) for the remediation of wastewater contaminated with metal complexes. *Environmental Engineering Research,* 20 (1) (2015) 89-97.

B. Conference / Seminar

1. **Lalsaimawia sailo**, Lalramnghaki Pachuau, Diwakar Tiwari. Treatment of wastewater Contaminated with Cu(II)-Iminodiacetic acid (IDA) complex species using Ferrate(VI). National Seminar on Horticulture for livelihood security, economic prosperity and sustainable development on 24th-26th September, 2012 which was organised by Department of Horticulture, Aromatic and medicinal Plants, Mizoram University, Aizawl, Mizoram.

2. Lalramnghaki Pachuau, **Lalsaimawia sailo**, Diwakar Tiwari. Fe(VI): An efficient and green oxidant in the treatment of wastewaters contaminated with Cu(II)-IDA complex species. 2nd International Conference on Advanced Oxidation Processes(AOP 2012) on 5th-8th October, 2012 which was organized by Society of Environmental Chemistry and Allied Sciences (SECAS) in Kottayam, India.

3. **Lalsaimawia sailo**, Lalramnghaki Pachuau, Diwakar Tiwari. Fe(VI): A Green chemical for the treatment of Cd(II)-Iminodiacetic acid (IDA) complex in aqueous wastes.

National Seminar on Green Chemistry for Greener Environment on 26th-27th November, 2012 which was organized by Department of Chemistry, Pachhunga University College, Mizoram University, Aizawl.

4. **Lalsaimawia Sailo**, Diwakar Tiwari. Application of ferrate(VI) in the treatment of aqueous wastes containing endocrine disrupting chemical bisphenol A. International Conference on Green Energy and smart materials through science, Technology and management (GESM'14) on 21st–23rd January, 2014 which was organized by Gauhati University (GU) and University of South Africa (UNISA) in Gauhati, Assam, India.

5. **Lalsaimawia Sailo**, Diwakar Tiwari. Applicability of ferrate(VI) in the oxidation of bisphenol A and diclofenac from aqueous wastes: Batch reactor operations. International Conference on Harnessing Natural Resources for sustainable Development : Global Trend on 29th–31st January, 2014 which was organized by Cotton College, Guwahati, Assam, India.

6. **Lalsaimawia Sailo**, International Conference cum exhibition on Drugs Discovery and Development from natural resources, 5th & 6th February, 2014 which was organized by Department of Pharmacy, RIPANS in Aizawl, Mizoram.

7. **Lalsaimawia Sailo**, Diwakar Tiwari, Seung Mok Lee. Ferrate(VI) : A green chemical in the treatment of aqueous waste contaminated with some endocrine disrupting chemicals (EDCs). Orientation Workshop on Radiation-Its Applications in Chemical, Physical and Life Sciences on 29th-31st October, 2014 which was organized by UGC-DAE Consortium for Scientific Research, Kolkata Centre & Department of Chemistry, Mizoram University.

Appendix

PUBLISHED JOURNAL PAPERS

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Highlights
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Keywords
1. Introduction
2. Materials and methods
3. Results and discussion
4. Conclusions
Acknowledgement
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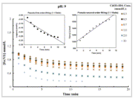
Figures and tables



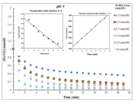


Table 1

Table 2

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Remediation of aquatic environment contaminated with the iminodiacetic acid metal complexes using ferrate(VI)

Diwakar Tiwari, Lalsaimawia Sailo, Lalramnghaki Pachuau

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Highlights

- M(II)-IDA complexed species in aqueous solutions are treated with Fe(VI) at various pH conditions.
- Kinetics of degradation is discussed.
- Mineralization of IDA is obtained with simultaneous removal of Cd(II) and Ni(II).

Abstract

The aim of this investigation is to assess the applicability of ferrate(VI) in the treatment of M(II)-complexed species *viz.*, Cd(II)-IDA and Ni(II)-IDA from aqueous solutions. The batch reactor operations are performed for various physico-chemical parametric studies. The batch reactor studies indicate that a fast and efficient decomplexation/removal of Cd(II)/Ni(II)-IDA is occurred at varied molar concentrations (0.3–10.0 mmol/L) of the complexed species treated with a constant dose of Fe(VI) (i.e., 1.0 mmol/L). Moreover, decreasing the pH values from 10.0 to 8.0 is further favored the decomplexation/degradation of these pollutant species. The time dependence data is utilized further in demonstrating the kinetic studies conducted for various molar ratios of M(II)-IDA to Fe(VI) as studied at different pH values (i.e., pH 10.0–8.0). The kinetic results show that the decomplexation/oxidation of complexed species is followed with pseudo-first and pseudo-second order rate kinetics for both the systems studied. Further, these results indicate that the rate of decomposition is followed with first order rate kinetics for both the reactants i.e., Fe(VI) and M(II)-IDA species. This infers that a 1:1 stoichiometry prevails to the decomposition M(II)-IDA species by Fe(VI). The overall rate constant values indicate that decreasing the pH causes to increase the rate of degradation/decomplexation of M(II)-IDA by Fe(VI). Decomplexation/oxidation of the complexes shows that a significant degradation/oxidation of the IDA occurred since a significant decrease in total organic carbon (TOC) is obtained. Again, lower pH values favor the oxidation/mineralization of IDA. Remarkably, a significant removal of free cadmium or nickel is obtained simultaneously. The removal of metal ions is further enhanced raising the pH of the Fe(VI) treated samples to 12.0 and almost 100% of Cd(II) was removed whereas a significant percent of Ni(II) was also removed. These results indicate that the treatment of aqueous wastes contaminated with M(II)-IDA is efficient and effective by Fe(VI).

Keywords

Ferrate(VI); M(II)-IDA; pH; Mineralization; Kinetics; Removal

1. Introduction

In marine and aquatic chemistry, heavy metals are not entirely free but usually occur as a range of metal complexed species [1] and [2]. Synthetic organic ligands such as APCAs (aminopoly carboxylic acids); containing carboxylic groups with one or more nitrogen

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Remediation of aquatic environment contaminated with the iminodiacetic acid metal complexes using ferrate(VI)

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ABSTRACT

The aim of this investigation is to assess the applicability of ferrate(VI) in the treatment of M(II)-complexed species *viz.*, Cd(II)-IDA and Ni(II)-IDA from aqueous solutions. The batch reactor operations are performed for various physico-chemical parametric studies. The batch reactor studies indicate that a fast and efficient decomplexation/removal of Cd(II)/Ni(II)-IDA is occurred at varied molar concentrations (0.3–10.0 mmol/L) of the complexed species treated with a constant dose of Fe(VI) (i.e., 1.0 mmol/L). Moreover, decreasing the pH values from 10.0 to 8.0 is further favored the decomplexation/degradation of these pollutant species. The time dependence data is utilized further in demonstrating the kinetic studies conducted for various molar ratios of M(II)-IDA to Fe(VI) as studied at different pH values (i.e., pH 10.0–8.0). The kinetic results show that the decomplexation/oxidation of complexed species is followed with pseudo-first and pseudo-second order rate kinetics for both the systems studied. Further, these results indicate that the rate of decomposition is followed with first order rate kinetics for both the reactants i.e., Fe(VI) and M(II)-IDA species. This infers that a 1:1 stoichiometry prevails to the decomposition M(II)-IDA species by Fe(VI). The overall rate constant values indicate that decreasing the pH causes to increase the rate of degradation/decomplexation of M(II)-IDA by Fe(VI). Decomplexation/oxidation of the complexes shows that a significant degradation/oxidation of the IDA occurred since a significant decrease in total organic carbon (TOC) is obtained. Again, lower pH values favor the oxidation/mineralization of IDA. Remarkably, a significant removal of free cadmium or nickel is obtained simultaneously. The removal of metal ions is further enhanced raising the pH of the Fe(VI) treated samples to 12.0 and almost 100% of Cd(II) was removed whereas a significant percent of Ni(II) was also removed. These results indicate that the treatment of aqueous wastes contaminated with M(II)-IDA is efficient and effective by Fe(VI).

1. Introduction

In marine and aquatic chemistry, heavy metals are not entirely free but usually occur as a range of metal complexed species [1,2]. Synthetic organic ligands such as APCAs (aminopoly carboxylic acids); containing carboxylic groups with one or more nitrogen atoms are able to complex with heavy metal ions. They are forming a few stable heteroatom rings through the phenomenon known as *chelating*. Existence of these complexes in water bodies causes serious environmental concerns due to some undesired features of the chelating agents such as their persistence or slow transformation in the environment, remobilization of toxic metal ions mainly from sediments and soils including with the radionuclides from radioactive waste into the aquatic environment [3]. It is stressed that most of the APCAs (*viz.*, EDTA – ethylene diaminetetraacetic acid, NTA – nitrilotriacetic acid, IDA – iminodiacetic acid, DTPA – diethylenetriamine penta-acetic acid) are resistant to conventional biological and physicochemical methods of waste water treatment and purification of drinking water. Such metal complexed species are found to be soluble over the entire pH region and showed an enhanced mobility of in aquatic environment [4]. Therefore, the presence of these metal complexed species in wastewater samples needs to be treated adequately prior to its ultimate discharge into the aquatic environment.

Iminodiacetic acid (IDA) is one of common chelating agent; often to be used in various industries. This enters into the aquatic environment through the discharge of untreated or partially treated industrial wastes. IDA is a promising sequestering agent hence widely employed in controlling the mobility of heavy metal toxic ions in the aquatic environment [5,6]. The other industrial applications of IDA are reported as in the detergent industry used

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as substitutes of phosphates [7,8]; chelating agents contained with IDA under different commercial products, *viz*., Amberlite IRC 748, Purolite S930, Lewatit TP 207 or Chelex-100, are also used in the speciation or trapping of several heavy metal ions. This is also used in making the functionalized carbon nanotubes which shows an enhanced applicability in the sorption, pre-concentration of several heavy metal cations in a heterogeneous separation process [9]. This is one of known chemical intermediates for the production of glycophosphate herbicides, electroplating solutions, chelating resin, surfactants, anticancer drugs, etc. [10–14]. The enhanced level of IDA and its complexed forms in the aqueous wastes combined with its toxicity, solubility and mobility in aqueous phases are caused serious environmental concerns. Therefore, an effective means of its removal has become a research endeavor. Although variety of chemicals and methods are proposed or employed in such wastewater treatment, but because of several environmental and health associated problems [15–17], there is a constant search for more viable, effective and eco-friendly alternative chemicals. Ferrate(VI) is a promising and perhaps an ideal substitute over the other oxidants due to its relatively higher oxidizing capacity, efficiency in disinfection and coagulation. It is an emerging water-treatment disinfectant and coagulant, which can address the concerns of disinfectant by-products (DBPs) associated with currently used chemicals such as free chlorine, chloramines, and ozone [16,18–25].

Ferrate(VI) is employed in the degradation/decomplexation of metal complexed species with simultaneous removal of metallic impurities from aqueous wastes [26–30]. Further it was employed in the treatment of electroplating industry waste contained with Cu(II) and Ni(II) complexed cyanides [30]. Cu(II)–EDTA complexed species was treated with Fe(VI) and indicated that a low pH conditions favored the decomplexation/degradation of these pollutants [31]. The polycarboxylic acids complexes *viz*., Zn(II)-NTA, Cd(II)-NTA are treated with Fe(VI) and showed that NTA is degraded significantly with simultaneous removal of Zn(II) or Cd(II). Further, the presence of several background electrolyte concentrations is studied in this treatment [32,33]. The study was extended for the suitability of Fe(VI) in the treatment of Cu(II) complexes with IDA, NTA, EDTA and EDDA and the order of oxidation is as: Cu(II)-EDDA > Cu(II)-IDA $\gg$ Cu(II)-NTA $\sim$ Cu(II)-EDTA which is in accordance to their respective stability constant values [34]. The sulfide mine tailings having metal complexed sulfides are treated with Fe(VI) and results show that the sulfide is oxidized rapidly to sulfate [35]. A similar simulated study is performed in the metal–sulfide treatment [36] and shows a fast oxidation is affected greatly in presence of $NaNO_2$ and Na_2SO_3 background electrolytes. Recent studies enabled to simulate the treatment of Cu(II)-IDA and Zn(II)-IDA species as a function of pH, concentration of pollutants as studied under the batch reactor operations [37]. The present investigation deals with the treatment of important IDA complexed species *viz*., Cd(II)-IDA and Ni(II)-IDA from aqueous solutions using the Fe(VI) as an alternative safe and relatively green chemical. The study is greatly extended to discuss various physico-chemical parametric studies including with solution pH, concentration of pollutants or Fe(VI) dose.

2. Materials and methods

2.1. Chemicals and apparatus

Iminodiacetic acid ($C_4H_7NO_4$), iron(III) nitrate nanohydrate ($Fe(NO_3)_3{\cdot}9H_2O$), diethyl ether ($C_4H_{10}O$), hexane (C_6H_{14}) were procured from Sigma Aldrich Co., USA. Potassium hydroxide (KOH), nickel(II) sulfate heptahydrate ($NiSO_4{\cdot}xH_2O$), hydrochloric acid (HCl), phosphoric acid (H_3PO_4) were obtained from Merck India Ltd., India. Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) was procured from the Loba Chemie, India. Moreover, the disodium tetraborate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$), disodium hydrogen phosphate (Na_2HPO_4) was obtained from Himedia India Ltd., India. Purified sodium hypochlorite (NaClO) was obtained from Palanad Enterprises, Nagpur, India. Purified water (10–15 MΩ cm) was obtained from Millipore Water Purification system (Model: Elix 3). Standard solutions of cadmium and nickel (1000 ppm) were obtained from Merck. These solutions were diluted and used for calibration of AAS (Atomic Absorption Spectrometer).

Glass filtration system with fritted funnel (10–15 μm) was obtained from Merck, India Ltd. and Whatman Filter Papers (GF/C grade, 47 mm) were used for filtration during ferrate(VI) preparation. Syringe filter of 25 mm diameter in size and porosity of 0.47 μm was obtained from Whatman, USA which was used for treated samples filtration. Electronic balance (Sartorius, BSA 224S-CW) was used for taking weights of chemicals. A pH-meter having glass and calomel electrode assembly (EUTECH Instruments; Model: Cyberscan pH 310, pH/MV/°C/°F Data meter) was used for entire pH measurements in aqueous solutions. Before using the pH meter, it was calibrated with the available buffer solutions.

2.2. Experimental

2.2.1. Preparation of potassium ferrate(VI)

Ferrate(VI) is prepared by adopting wet chemical oxidation method, with some modifications as described elsewhere [30,38]. Ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) is treated with sodium hypochlorite (NaClO) containing higher percent of free chlorine (12–14%) under very cold and highly alkaline environment; Fe(III) is oxidized to Fe(VI) and precipitated in the form of slurry K_2FeO_4 which is further purified by repeating re-crystallization for 3–4 times. The purity of Fe(VI) was assessed by UV–Visible measurement using the known standard molar extinction coefficient of Fe(VI) solution $1150\ M^{-1}\ cm^{-1}$ at 510 nm at pH $\sim$ 9.2 [39]. The purity of the prepared ferrate(VI) is thus found to be above 95%. The product is carefully kept in a vacuum desiccator contained with NaOH pellets.

2.2.2. Analytical methods

UV–Visible measurements along with TOC (total organic carbon) analysis enable to study the decomplexation or degradation of Cd(II)/Ni(II)-IDA complexed species present in simulated wastewaters by ferrate(VI). Batch experiments are performed by treating different concentrations of IDA metal complexes (0.3–10.0 mmol/L of Cd(II)-IDA and Ni(II)-IDA) with a constant dose of Fe(VI), i.e., 1.0 mmol/L and at varied pH conditions (i.e., pH 8.0, 9.0 and 10.0). The decomposition in Fe(VI) is obtained in correlation with the degradation of the IDA complexes under study. The wastewater samples, once introduced with Fe(VI) are immediately subjected to measure the absorbance of the solution recorded at 510 nm at regular interval of time for a total period of 20 min. Similarly, the absorbance of Fe(VI) blank solution is also recorded at the same pH values and for the same time intervals at 510 nm for necessary absorbance correction that occurs due to self-degradation of Fe(VI). Following with the UV–Vis analysis, the Fe(VI) treated solution mixtures are stirred for another 2 h and then filtered with 0.47 μm syringe filter. The filtrates are subjected for the TOC (total organic carbon) analyzer (Shimadzu, Japan; Model: TOC-VCPH/CPN) as to obtain the TOC values of the treated samples. Thereafter, the percent mineralization of IDA was obtained using the initial TOC values of the untreated samples.

The UV–Visible data obtained as a function of time is further utilized to study the kinetics involved in the oxidation of Cd(II)/NI(II)-IDA complexed species indirectly by the ferrate(VI) degradation.

Subsequent removal of the free metal ions in the treated sample solutions by Fe(VI) was further obtained and studied. Part of the filtrate samples obtained above are taken and divided into two portions. One portion of the filtrate samples are subjected to the AAS analysis using Flame Atomic Absorption Spectrophotometer (Perkin-Elmer, Analyst 200) for quantitative estimation of total dissolved metal ions, i.e., Cd(II) or Ni(II) ions. The pH of other portions of the filtrate samples is raised to 12.0 so as to investigate the effect of enhanced coagulation or precipitation at higher pH values on the removal of metallic species from solutions. The filtrate samples at pH 12 are filtered using 0.47 μm syringe filter and the AAS data for the total metal concentrations are again recorded. The percent removal of metals is finally estimated against the total metal concentrations recorded for each treated samples and that of the corresponding untreated samples concentration at the studied pHs.

3. Results and discussion

3.1. Decomplexation/degradation of Cd(II)/Ni(II)-IDA complexes by ferrate(VI)

3.1.1. Effect of pH and concentration of Cd(II)/Ni(II)-IDA complexes

The UV–Visible analysis is performed to study the decomplexation/degradation of Cd(II)/Ni(II)-IDA complexes treated with Fe(VI). Different molar concentrations of Cd(II)/Ni(II)-IDA, i.e., from 0.3 to 10.0 mmol/L are treated with a constant dose of Fe(VI), i.e., 1.0 mmol/L at different pH values ranging from pH 8.0 to 10.0. The reduction in Fe(VI) concentration is obtained which indicates that the IDA complexes are decomplexed or degraded when treated with Fe(VI). The change in Fe(VI) concentration as a function of time for different Cd(II)/Ni(II)-IDA concentrations are calculated from the absorbance of the solutions recorded at 510 nm and at pH values of 8.0, 9.0 and 10.0. The results obtained at pH 9.0 are presented in Figs. 1 and 2 respectively for Cd(II)-IDA and Ni(II)-IDA. The results infer that Fe(VI) is decomposed quite rapidly and significantly in presence of Cd(II)/Ni(II)-IDA complexes and that the effect is highly dependent to pH of solution, reaction time and concentration of the complexes. The figures (Figs. 1 and 2) clearly demonstrated that the Fe(VI) is degraded rapidly in presence of Cd(II)/Ni(II)-IDA during initial period of contact time and just within *ca.* 5–10 min of contact it reaches to almost a constant values of Fe(VI) concentration. Quantitatively, within initial 5 min, the Fe(VI) removal is as high as ~75–95% for various molar concentrations of Ni(II)-IDA at pH 8.0. Similarly, for the system of Cd(II)-IDA with concentration of 10.0 mmol/L at pH 8.0, it took 7 min of contact time to attain an apparent equilibrium as no further decrease in Fe(VI) concentration is recorded. This fast initial degradation of Fe(VI) is in general enhanced with decreasing the pH from pH 10.0 to 8.0 which is well explicable to the fact that the redox potential of Fe(VI) is significantly high at lower pH values (2.20 and 0.72 at pH 1 and pH 14, respectively). It is further observed that increasing the molar concentration of Ni(II)-IDA, in general, favors the decomplexation/degradation of Ni(II)-IDA species in solutions since an enhanced rate of decomposition of Fe(VI) is obtained. Increasing the concentration of Ni(II)-IDA from 0.3 mmol/L to 10.0 mmol/L, the corresponding percent decomposition of Fe(VI) was increased from 92.16% to 100% within 20 min of contact time at pH 9.0. Similarly, for the system of Cd(II)-IDA, the increase is from 48.40% to 76.75% at the same pH value. The increase in degradation of Fe(VI) with increase in concentration of the IDA complexes is again more pronounced at lower pH values illustrating that acidic conditions favored decomplexation of Ni(II)-IDA complexes in presence of Fe(VI). Several authors reported similar observations for other metal organo complexed systems elsewhere [32,37,31].

3.1.2. Kinetics of Cd(II)/Ni(II)-IDA decomplexation/degradation

The kinetics involved in the removal of Fe(VI), in presence of various concentrations of Cd(II)/Ni(II)-IDA at different pH values, are carried out by utilizing the time dependence absorbance data collected at different pH values and molar ratios of Fe(VI) to Cd(II)/Ni(II)-IDA. The absorbance data is corrected for the self-decomposition of Fe(VI) using the blank run and then normalized to the Fe(VI) concentration. Further, this was utilized in the rate calculations. It was earlier reported that the decomposition of Fe(VI) into Fe(III) through the following reductive pathways [37,40]:

$$2\mathrm{FeO_4^{2-}} + 3\mathrm{H_2O} \rightarrow 2\mathrm{Fe(OH)_3} + 5[\mathrm{O}] \tag{1}$$

$$[\mathrm{O}] + \mathrm{H_2O} \rightarrow 2{\cdot}\mathrm{OH} \tag{2}$$

$$2{\cdot}\mathrm{OH} \rightarrow \mathrm{H_2O_2} \tag{3}$$

$$2\mathrm{H_2O_2} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} \tag{4}$$

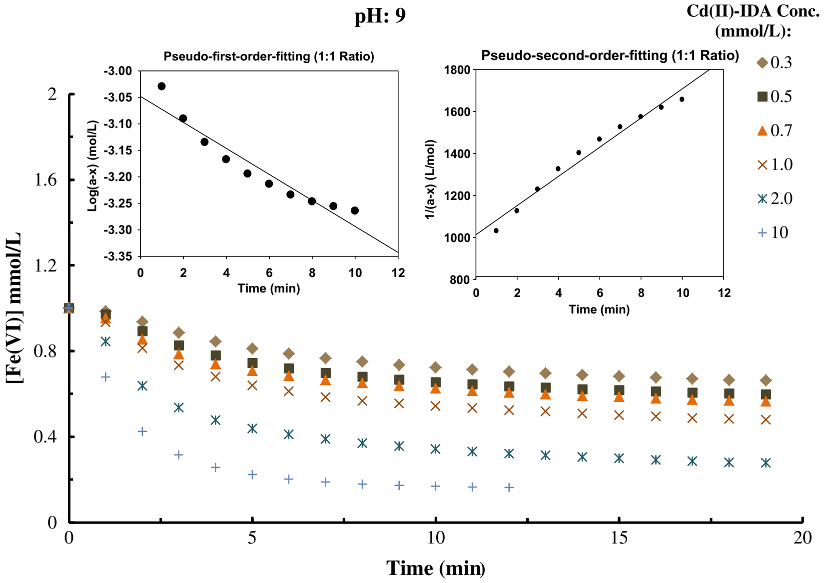

Fig. 1. Degradation of IDA in presence of Fe(VI) as a function of time for different concentrations of Cd(II)-IDA at constant pH:9.0 [initial conc. of Fe(VI): 1.0 mmol/L].

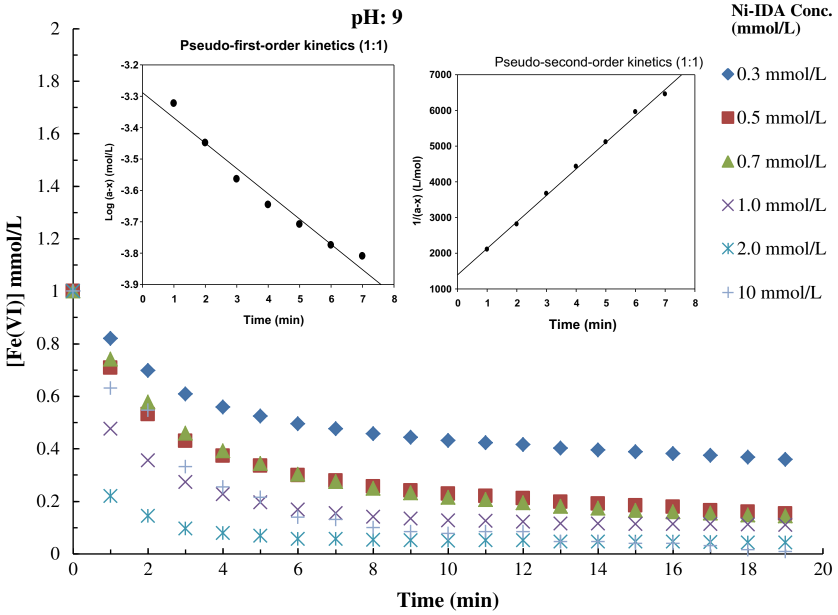

Fig. 2. Degradation of IDA in presence of Fe(VI) as a function of time for different concentrations of Ni(II)-IDA at constant pH:9.0 [initial conc. of Fe(VI): 1.0 mmol/L].

With this the hydroxyl free radical generated is one of strong oxidizing agent [41] which may likely to decomplex/degrade the pollutants in aqueous solutions. The simple kinetics in the degradation of Cd(II)/or Ni(II)-IDA is discussed by the change in Fe(VI) concentrations using the absorbance data collected at 510 nm wave length. The basic equation for the reduction of Fe(VI) in presence of M(II)-IDA may be represented as:

$$\mathrm{Fe(VI)} + \mathrm{M(II)\text{-}IDA} \rightarrow \mathrm{Fe(III)} + \text{Oxidized Products} + \mathrm{CO_2} + \mathrm{N_2} \quad (5)$$

It is assumed that partly/or fully the decomplexed IDA mineralized to its end products, which is analyzed by the TOC values. Moreover, the self-decomposition of ferrate(VI) is even significant at the studied pH values [30,39] is therefore excluded by necessary correction performed by the blank corrections conducted at the same pH conditions. The rate of decomposition of ferrate(VI) is expressed as:

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k[\mathrm{Fe(VI)}]^m[\mathrm{Cd(II)/or\ Ni(II)\text{-}IDA}]^n \quad (6)$$

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k_1 \times [\mathrm{Fe(VI)}]^m \quad (7)$$

$$\text{where, } k_1 = k[\mathrm{Cd(II)/or\ Ni(II)\text{-}IDA}]^n \quad (8)$$

The time dependence change in Fe(VI) concentration is utilized to fit in the Eq. (7) to optimize the value of $m = 1$ or 2 as employing the pseudo-first and pseudo-second order equations and the results are presented graphically in Figs. 1 and 2 as in insets, respectively for the Cd(II)-IDA and Ni(II)-IDA systems (e.g., at pH 9.0 with 1:1 M ratio with Fe(VI)). The rate constants along with the R^2 values estimated both for the pseudo-first and pseudo-second-order are returned in Tables 1 and 2, respectively for Cd(II)-IDA and Ni(II)-IDA as studied for varied molar ratios and at different pH values. Results show that the rate constant is decreased significantly with the increase in pH from 8.0 to 10.0 clearly indicating that the rate of removal of Fe(VI) or the degradation of Cd(II)/Ni(II)-IDA is more pronounced at lower pH values. Quantitatively, decreasing the pH from 10.0 to 8.0, the rate constant is increased, respectively from 5.99×10^{-2} to $14.28 \times 10^{-2}\ \mathrm{min}^{-1}$ (for pseudo-first-order) and from 45.93 to 113.2 L/mol/min (for pseudo-second-order) at the 1:1 M ratios of Fe(VI) and Cd(II)-IDA. Again, in case of Ni(II)-IDA system, decreasing the pH from 10.0 to 8.0 the rate constant is increased, respectively from 11.28×10^{-2} to $55.73 \times 10^{-2}\ \mathrm{min}^{-1}$ (for pseudo-first-order) and from 143.2 to 2640.0 L/mol/min (for pseudo-second-order) at the 1:1 M ratios of Fe(VI) and Ni(II)-IDA. It is observed that the rate of decomposition of Fe(VI) is significantly higher at lower pH values, this is because of the enhanced reactivity of Fe(VI) at lower pH values [18,22]. These results are in a line with the other studies conducted towards the decomposition of other complex species by Fe(VI) [37].

The overall rate constant 'k' (Eq. (6)) is estimated with the help of Eq. (8). The values of k_1 at different concentrations of [M(II)-IDA] is plotted both for pseudo-first-order and pseudo-second order rate constant values. Moreover, the value of 'n' is also estimated for its possible values of 1 and 2; but the data is best fitted both for $m = 1$ and for $n = 1$ as fairly a high value of R^2 is obtained for these two systems at various pH conditions (cf. Fig. 3). Therefore, using these plots, the overall rate constant values (k) is obtained from the slope of these lines. Further, the values of k along with the R^2 values are returned in Table 3 both for the Cd(II)-IDA and Ni(II)-IDA systems. In general, increasing the pH from 8.0 to 10.0, the overall rate constant was decreased. As pH is increased from 8.0 to 10.0, the overall rate constant is found to be decreased from 126.7 to 51.7 L/mol/min for Cd(II)-IDA and from 538.0 to 105.0 L/mol/min in case of Ni(II)-IDA. This is in accordance to the reactivity of Fe(VI) in solution as protonated species ($\mathrm{HFeO_4^-} \leftrightarrow \mathrm{H^+} + \mathrm{FeO_4^{2-}}$; $\mathrm{p}K_a^2 = 7.3$) possesses larger spin density than the deprotonated species and shows an enhanced reactivity [42,43]. It is also demonstrated that 1:1 stoichiometry is occurred in the decomplexation/degradation of M(II)-IDA with Fe(VI). Previously, it was reported that the degradation of thiocyanate by Fe(VI) was found to be pseudo-first order with respect to the Fe(VI). Therefore, the rate constants (k_1) at various concentrations of thiocyanate were evaluated [44]. Further, the plot between k_1 versus $\mathrm{SCN^-}$ concentrations is found to be linear, hence, suggested that the rate law for this reaction was first order with respect to $\mathrm{SCN^-}$ as well. The rate of reactions was increased with decreasing the pH. This inferred that protonation of Fe(VI) caused to enhance the reactivity of the Fe(VI). Similar results were also reported for the decomposition of Cu(I)–cyanide complex systems [45].

Table 1
Pseudo-first and pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentration of Cd(II)-IDA at different pH conditions.

[Cd(II)-IDA] (mmol/L)	Pseudo-first-order rate constant ($\times 10^{-2}$) (1/min)						Pseudo-second-order rate constant (L/mol/min)					
	pH 8.0		pH 9.0		pH 10.0		pH 8.0		pH 9.0		pH 10.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.3	5.06	0.954	2.99	0.951	2.07	0.941	46.80	0.942	25.84	0.921	26.58	0.963
0.5	5.98	0.943	3.45	0.913	2.99	0.932	62.19	0.935	37.45	0.912	31.07	0.938
0.7	7.59	0.944	4.14	0.907	3.22	0.917	76.03	0.929	38.42	0.903	31.59	0.913
1.0	14.28	0.947	7.37	0.929	5.99	0.906	113.2	0.951	50.08	0.902	45.93	0.939
2.0	24.87	0.935	15.89	0.902	9.90	0.911	265.3	0.971	120.8	0.933	102.0	0.962
5.0	25.56	0.924	19.57	0.907	14.9	0.931	461.1	0.891	376.5	0.927	207.1	0.995
10.0	29.70	0.970	20.03	0.902	14.2	0.935	417.7	0.912	450.4	0.919	315.2	0.997
15.0	21.64	0.962	19.11	0.915	14.0	0.963	410.2	0.986	412.6	0.964	168.8	0.994

Table 2
Pseudo-first and pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentrations of Ni(II)-IDA at different pH conditions.

[Ni(II)-IDA] (mmol/L)	Pseudo-first-order rate constant ($\times 10^{-2}$) (1/min)						Pseudo-second-order rate constant (L/mol/min)					
	pH 8.0		pH 9.0		pH 10.0		pH 8.0		pH 9.0		pH 10.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.3	24.87	.955	5.98	0.898	3.99	0.874	1150	.993	117.3	0.953	49.04	0.919
0.5	27.41	.852	7.13	0.905	4.37	0.938	1389	.935	265.9	0.988	79.39	0.980
0.7	34.55	.895	9.21	0.924	5.06	0.941	2273	.914	311.2	0.991	101.3	0.986
1.0	55.73	.912	18.42	0.964	11.28	0.987	2640	.990	521.8	0.952	143.2	0.981
2.0	48.13	.971	29.24	0.951	21.64	0.935	5991	.866	1933	0.948	293.3	0.942
10.0	53.43	.961	32.24	0.96	11.28	0.914	3829	.939	1092	0.952	185	0.915

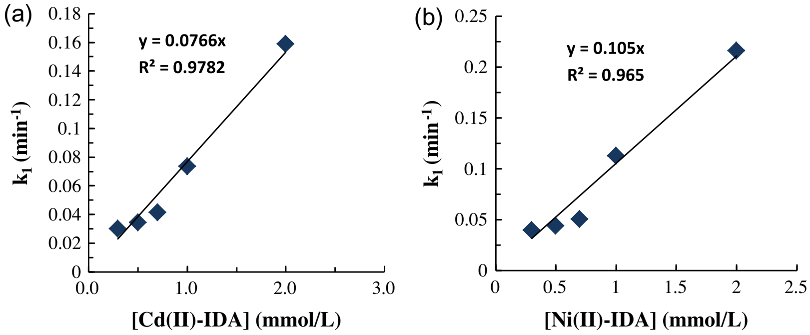

Fig. 3. Fitting of pseudo-first-order rate constant values with different concentrations of (a) Cd(II)-IDA; and (b) Ni(II)-IDA.

Table 3
Overall rate constant in the decomplexation/degradation of M(II)-IDA by ferrate(VI) at different pH conditions.

pH	Cd(II)-IDA system		Ni(II)-IDA system	
	k (L/mol/min)	R^2	k (L/mol/min)	R^2
8.0	126.7	0.9775	538.0	0.968
9.0	76.6	0.9782	152.0	0.958
10.0	51.7	0.9641	105.0	0.965

3.2. Mineralization of IDA

The oxidation of IDA followed with the decomplexation of Cd(II)/or Ni(II)-IDA complexes by Fe(VI) is also investigated with the help of TOC measurements. The total organic carbon data are obtained for various stoichiometric ratios of Fe(VI) and Cd(II)/Zn(II)-IDA (1:0.3–1:10) treated at different pH conditions i.e., pH 8.0–10.0. Results are presented graphically in Figs. 4 and 5, respectively for the Cd(II)-IDA and Ni(II)-IDA systems. The results demonstrated that organic IDA species is effectively degraded/mineralized by Fe(VI). In fact, IDA is completely mineralized for most of the concentrations of Ni(II)-IDA and Cd(II)/IDA, i.e., up to 1:1 stoichiometric ratio of Fe(VI) and Cd(II)/or Ni(II)-IDA. However, at higher concentrations of M(II)-IDA, the degradation of IDA are lowered significantly at all the studied pH conditions. This demonstrates that Fe(VI) is able to oxidize IDA more effectively at lower concentrations of the IDA complexed species. Overall, it is cleared from the figures again that increasing the pH from 8.0 to 10.0, the TOC percent removal is decreased from 26.11% to 19.17% and 41.80% to 22.60%, respectively for 1:10 M ratios of Fe(VI): Ni(II)-IDA and Fe(VI): Cd(II)-IDA. Therefore, the TOC data confirms the degradation of organic species of IDA from Cd(II)/Ni(II)-IDA complexes by Fe(VI) treatment is favored at lower pH conditions which is in a line to the previously observed UV–Vis data. Other organic compounds such as naphthalene and trichloroethylene are also reported to be completely mineralized by the Fe(VI) [46]. The other studies enables that increasing the Fe(VI) dose (ferrate(VI):BPA (bisphenol A) ratio) the value of DOC (dissolved organic carbon) is decreased from 60% to 20% i.e., an extent of mineralization increased systematically. They have also concluded that, since the degrees of degradation and mineralization for Fe(VI):BPA ratios is found greater than 1, indicating that some intermediates of BPA is formed but with the time, the intermediates are also degraded/oxidized and mineralized [38].

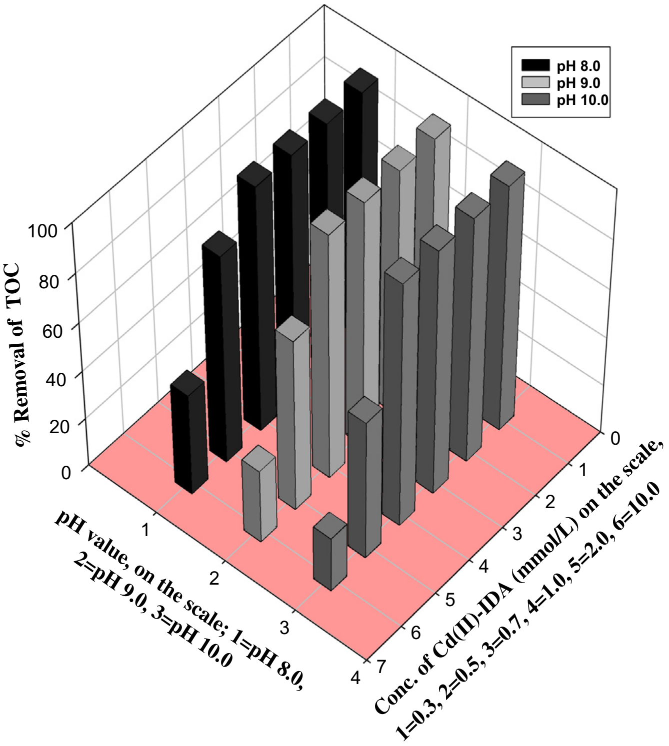

Fig. 4. Mineralization of IDA for different concentrations of Cd(II)-IDA treated with Fe(VI) of 1.0 mmol/L at different pH values.

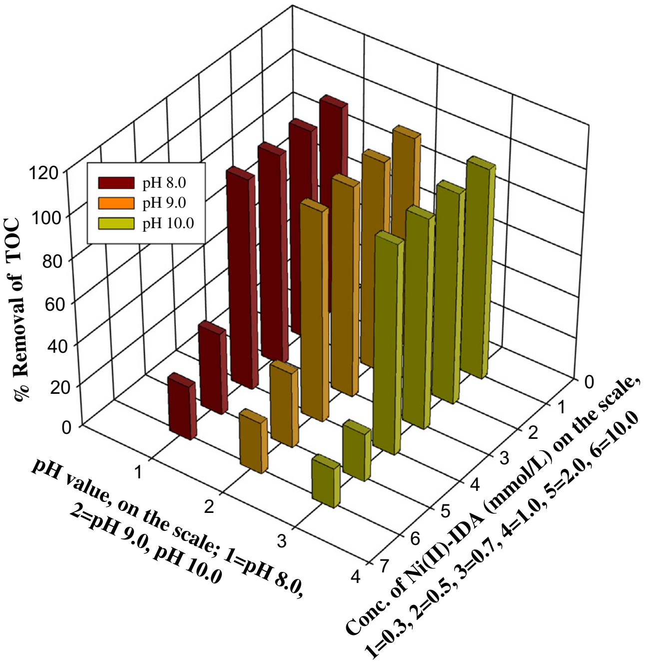

Fig. 5. Mineralization of IDA for different concentrations of Ni(II)-IDA treated with Fe(VI) of 1.0 mmol/L at different pH values.

3.3. Simultaneous removal of Cd(II)/Ni(II) ions

The simultaneous removal of Cd(II)/Ni(II) from the treated sample solutions through coagulation/adsorption by Fe(VI) is further investigated by ASS analysis. Several studies have indicated that the reduced Fe(III) acts as an excellent coagulant/adsorbent in the wastewater treatment; hence, keeping in view, the simultaneous removal of Cd(II) or Ni(II) from treated aqueous solutions are studied. The Fe(VI) treated samples are filtered and part of this sample is subjected to increase its pH to 12.0 by the drop wise addition of conc. NaOH solutions. Further, both the fraction of samples is subjected for the AAS measurements. The removal of Cd(II) or Ni(II) by the Fe(VI) treatment is presented graphically in Figs. 6 and 7, respectively for Cd(II) and Ni(II). The data indicates that relatively insignificant percent removal of Cd(II) and Ni(II) is occurred at lower pH values, especially for the higher concentrations of Ni(II)-IDA. However, once the treated samples pH is raised to 12.0, a remarkable sharp increase in percent removal of Cd(II) and Ni(II) is obtained even for higher molar concentrations of Cd(II)/Ni(II)-IDA. At low pH 8.0, maximum percent of metal ion removal is obtained as 21.05% for 0.3 mmol/L of Ni(II)-IDA, whereas it is increased to 83.33% while raising the solution pH 12.0. It is observed that at elevated pH conditions the simultaneous removal of Ni(II) is greatly increased. Similarly, almost a

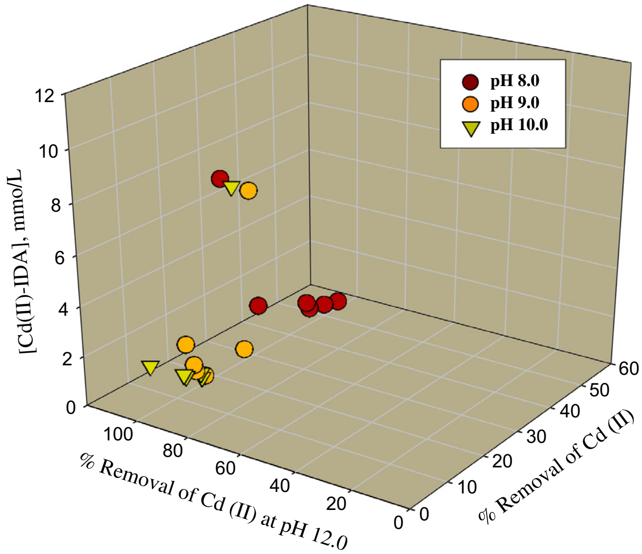

Fig. 6. Simultaneous removal of Cd(II) for different concentrations of Cd(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH values.

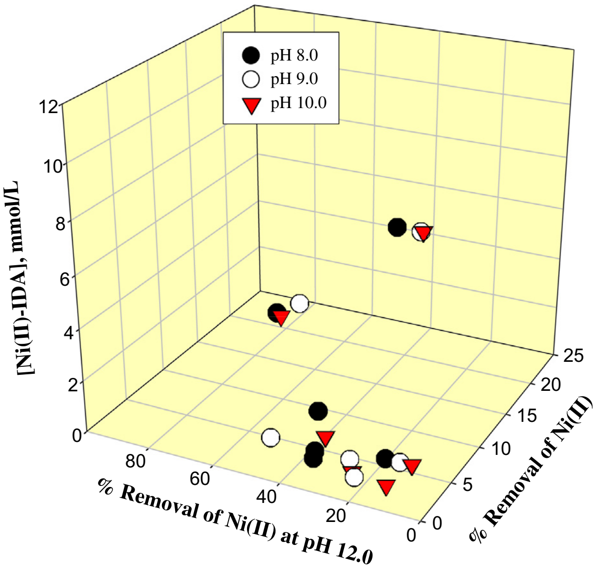

Fig. 7. Simultaneous removal of Ni(II) for different concentrations of Ni(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH values.

complete removal of Cd(II) is achieved for the Cd(II)-IDA systems. The enhanced removal of metals at elevated pH values i.e., at pH 12.0 is possibly due to the significant decrease in solubility of precipitate $Cd(OH)_2$ (s) or $Ni(OH)_2$ (s) species at higher pH values. Other studies also reported a complete removal of free copper in case of Cu(II)-cyanide complex and a partial removal of Ni(II) from Ni(II)-cyanide complex species was obtained [26].

4. Conclusions

Ferrate(VI) is 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 is obtained for various molar concentrations (0.3–10.0 mmol/L) of the complex species treated with a constant dose of Fe(VI) (i.e., 1.0 mmol/L). The efficiency of the Fe(VI) is increased further decreasing the solution pH from 10.0 to 8.0. Moreover, the kinetic studies are conducted employing the absorbance data at various pH values and at different molar ratios of the Fe(VI) to M(II)-IDA species. The kinetic results shows that decomplexation/oxidation of complex species follows pseudo-first and pseudo-second order rate kinetics for both M(II)-IDA species which further indicates that the rate of reaction is of first order both for the Fe(VI) and M(II)-IDA. This infers a 1:1 stoichiometry occurred for the Fe(VI) and M(II)-IDA species. Further, the overall rate constant shows that decreasing the pH values from 10.0 to 8.0 greatly enhances the rate of degradation/decomplexation of M(II)-IDA by Fe(VI). Further, a significant degradation/oxidation of the organic species i.e., IDA is occurred since a significant decrease in total organic carbon (TOC) is obtained for these systems. Again, lower pH values favor the oxidation/mineralization of IDA. Remarkably, a significant removal of free cadmium or nickel is obtained. The removal of metals is further enhanced raising the pH of the Fe(VI) treated samples to 12.0 and almost 100% of Cd(II) is removed whereas a significantly high percent of Ni(II) is removed simultaneously. These results shows that the Fe(VI) treatment is efficient and effective at least for the treatment of wastewaters contaminated with the Cd(II)-IDA or Ni(II)-IDA complex species.

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Efficient use of ferrate(VI) for the remediation of wastewater contaminated with metal complexes

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ABSTRACT

Remediation of wastewater contaminated with metal(II)-complexed species (Cu(II)-NTA (NTA: nitrilotriacetic acid), Cu(II)-EDTA (EDTA: ethylenediamine tetraacetic acid) and Cd(II)-EDTA is attempted using the potential applicability of ferrate(VI). Kinetics of pollutant degradation is obtained with the removal of ferrate(VI) studied at wide range of pH (8.0-10.0) and the concentration of metal(II)-complexed species (0.3 to 15.0 mmol/L) employing a constant dose of ferrate(VI) i.e., 1.0 mmol/L. Pseudo-first-order and pseudo-second-order rate constants were obtained in the reduction of ferrate(VI) which was then employed to obtain the overall rate constants of the pollutant degradation. The mineralization of NTA and EDTA was obtained with the change in TOC (total organic carbon) values collected by the ferrate(VI) treated pollutant samples. Decrease in pH and molar pollutant concentrations was greatly favored the percent mineralization of NTA or EDTA by the ferrate(VI) treatment. The treated pollutant samples were filtered and subjected for AAS (atomic absorption spectrophotometric) analysis to assess the simultaneous removal of copper and cadmium from aqueous solutions at the studied pH as well at the elevated pH 12.0. Results show that an enhanced removal of cadmium or copper was achieved at pH 12.0. Overall, ferrate(VI) possesses multifunctional application in wastewater treatment as it oxidizes the degradable impurities and removes metallic impurities by coagulation process.

Keywords: Coagulation, Ferrate(VI), Kinetics, Metal(II)-complexed species, Mineralization, Oxidation

1. Introduction

Metal-complexed species are widely employed for various industrial applications including metal finishing, painting, dying, photography, surface treatment, printed circuit board manufacturing etc. [1]. Mobility, bioavailability and toxicity of these pollutants are largely dependent to the speciation of these species present. It is further indicated that metal complexed species are highly mobile in aqueous solutions [2]. The presence of these metal complex species in aquatic environment creates a serious environmental concern since it get escapes from the wastewater treatment plants (WTP); hence poses serious issues relating to the biochemical hazards [3-5]. Several methods are demonstrated to remove these pollutants from aqueous solutions such as adsorption [6], Fe^{2+} replacement and precipitation [7, 8], ion exchange [9, 10], membrane filtration [11], electro-coagulation and deposition [12] etc. but are seemingly less or partial effective with these treatment processes.

Ethylenediamine tetraacetic acid (EDTA) is one of strong chelating agent forming relatively stable chelates with several metal cations including copper and cadmium. EDTA is widely employed in electrode-less copper-plating in the printed circuit boards (PCBs) [13-15], electroplating, paper manufacturing [16] and agricultural industries as a potential metal sequester [17, 18]. Similarly, nitrilotriacetic acid (NTA) is a class of synthetic aminopolycarboxylic acid (APCA) forming stable chelates with several metal cations which enables it to utilize in the industries like detergent builder where it chelates with magnesium and calcium ions and preventing the formation of scales. It is widely employed in the food industries, pharmaceuticals, cosmetic, metal finishing, photographic, textile, paper industries, nuclear decontamination etc. [19-22]. These industrial operations, therefore, poses a serious environmental threat due to the discharge of untreated or partially treated industrial wastes into the water bodies which ultimately contaminating the aquatic environment.

Higher oxidation state of iron i.e., ferrate(VI) is found to be a potential and useful oxidant. Ferrate(VI) possesses relatively higher redox potential as compared to commonly used oxidants hence; shows wide applications in the treatment of variety of

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water pollutants at low levels [23-29]. The use of ferrate(VI) in the wastewater treatment technologies shows multifunctional applicability since during initial stage of treatment, ferrate(VI) serves to oxidize the degradable impurities and in the latter stages the reduced ferric(III) coagulates or even adsorbs the non-degradable metallic impurities. Additionally, ferrate(VI) is also reported to be an efficient disinfectant [23, 26, 28, 29].

These promising properties of ferrate(VI) enables the chemical to degrade/or decomplex the metal complexed species with simultaneous removal of free metals from aqueous solutions [30-34]. It is successfully employed in the treatment of electroplating wastes contained with Cu(II) and Ni(II) complexed cyanides [34]. The polycarboxylic acid complexes *viz*., Zn(II)-NTA, Cd(II)-NTA are treated with ferrate(VI) and shows that NTA is degraded significantly with simultaneous removal of Zn(II) or Cd(II) from aqueous solutions. Further, the presence of several background electrolyte concentrations is studied in the treatment [35, 36]. The study is extended to assess the suitability of ferrate(VI) in the treatment of Cu(II)- iminodiacetic acid (IDA) or NTA or EDTA and ethylenediaminediacetic acid (EDDA) and the order of the oxidation is as: Cu(II)-EDDA > Cu(II)-IDA >> Cu(II)-NTA~Cu(II)-EDTA which is in accordance to their respective stability constant values [37]. The sulphide mine tailings having metal complexed sulphides are treated with ferrate(VI) and results show that the sulphide is oxidized rapidly to sulphate [38]. A similar simulated study is performed in the metal-sulphide treatment [39] and shows that a fast oxidation is affected greatly in presence of $NaNO_2$ and Na_2SO_3 background electrolytes. Recent studies enable to simulate the treatment of copper(II)-IDA and zinc(II)-IDA species as a function of pH, concentration of pollutants as studied under batch reactor operations [40]. Kinetics of ferrate(VI) reduction in the treatment of cadmium(II)-IDA and nickel(II)-IDA complexed species from aqueous solutions is demonstrated elsewhere [41]. The present investigation deals with the treatment of wastewaters contaminated with copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA metal complexed species using ferrate(VI) as an alternative safe and relatively green degradation process. The study is extended to discuss various physico-chemical parametric studies *viz*., the effect of pH and pollutant concentrations.

2. Materials and Methods

2.1. Materials

Nitrilotriacetic acid ($C_6H_9NO_6$), iron(III) nitrate nanohydrate ($Fe(NO_3)_3$. $9H_2O$), diethyl ether ($C_4H_{10}O$) and hexane (C_6H_{14}) are procured from Sigma Aldrich. Co., USA. Disodium ethylenediamine tetraacetic acid ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) and cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) are obtained from Loba Chemie, Pvt. Ltd., India. Potassium hydroxide (KOH), copper sulphate pentahydrate ($CuSO_4$ $\cdot5H_2O$), hydrochloric acid (HCl), phosphoric acid (H_3PO_4) is procured from Merck India Ltd., India. Moreover, the disodium tetraborate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$), disodium hydrogen phosphate (Na_2HPO_4) is obtained from Himedia India Ltd., India. Purified sodium hypochlorite (NaClO) is obtained from Palanad Enterprises, Nagpur, India. Purified water (10-15 MΩ cm) is obtained from Millipore Water Purification system (Model: Elix 3).

Glass filtration system having fritted funnel (10-15μm) is obtained from Merck India Ltd., India. Whatman Filter Paper (GF/C grade, 47mm; USA) is used for filtration during ferrate(VI) preparation. Syringe filter 25 mm diameter having porosity of 0.47 μm is obtained from Whatman, USA. This is used for ferrate(VI) treated samples filtration. Electronic balance (BSA 224S-CW; Sartorius) is employed for weighing purpose. A pH-meter having glass and calomel electrode assembly (Cyberscan pH 310; EUTECH Instruments, pH/MV/°C/°F Data meter) is used for entire pH measurements in aqueous solutions.

Ferrate(VI) is synthesized in laboratory by wet chemical oxidation method as described elsewhere [34, 35, 42]. The ferrate(VI) was obtained to its potassium salt form (K_2FeO_4).The purity of the synthesized potassium ferrate(VI) was found to be *Ca* 95%. The product is carefully kept in a vacuum desiccator containing excess pellets of sodium hydroxide.

2.2. Batch Reactor Operations

UV-visible measurements, in particular the change in ferrate(VI) concentrations, along with the TOC (total organic carbon) analysis clearly demonstrate to observe the decomplexation or degradation of Cu(II)/Cd(II)-complexed species present in simulated wastewaters by ferrate(VI). Batch reactor operations are performed by treating different concentrations of the metal-complex species (0.5 to 15.0 mmol/L of copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA with a constant dose of ferrate(VI), i.e., 1.0 mmol/L and at varied pH conditions (i.e., pH 8.0, 9.0 and 10.0). The decomposition of ferrate(VI) is obtained in correlation with the degradation of NTA/or EDTA complex species. A known quantity of ferrate(VI) is introduced with the pollutant solution and immediately the solution is subjected to the UV-visible spectrometer as to record the change in absorbance value. The absorbance is recorded at the wavelength of 510 nm and at a regular interval of times for a total period of 20 min. Similarly, the absorbance of ferrate(VI) blank solution is also recorded in parallel for making necessary blank corrections which occurs due to the self-decomposition of ferrate(VI). Following with the UV-Vis analysis, the ferrate(VI) treated samples are stirred for another 2 hrs at room temperature and then filtered with 0.47 μm syringe filter. The filtrates are subjected for its TOC analysis (TOC-VCPH/CPN; Shimadzu, Japan) so as to obtain the TOC values of the treated samples. Thereafter, the percent mineralization of NTA/or EDTA is calculated by using the initial TOC values of the untreated samples.

Moreover, the UV-visible data obtained as a function of time is further utilized to study the kinetics of the oxidation of metal(II)-complex species indirectly with the ferrate(VI) reduction to ferric(III) hydroxide.

The removal of free metal ions in the treated sample solutions by ferrate(VI) is further analyzed. The filtrates obtained by ferrate(VI) treated samples are divided into two portions. One portion of the filtrate samples are subjected to atomic absorption spectrophotometric (AAS) analysis (Flame Atomic Absorption Spectrophotometer, Perkin-Elmer, Analyst 200) for the quantitative estimation of total metals, i.e., copper(II) or cadmium(II). The pH of other portion of the filtrate is raised to 12.0 by the addition of conc. NaOH solution so as to investigate the effect of enhanced coagulation at higher pH values in the removal of metals from aqueous solutions. The samples at pH 12 are again filtered using 0.47 μm syringe filter and subjected to the AAS analysis as to obtain the total metal concentrations. The percent removal of metals is finally estimated.

3. Results and Discussion

3.1. Decomplexation/degradation of Metal(II)-complex Species by Ferrate(VI)

3.1.1. Effect of pH and concentration of metal(II)-complex species

Varied molar concentrations of metal(II)-complex solutions i.e., from 0.5 to 15.0 mmol/L at different pH values (pH 8.0 to 10.0) are taken in a reaction reactor. The known amount of the solid K_2FeO_4 is added in reactor as to obtain a constant dose of ferrate(VI), i.e., 1.0 mmol/L. The reduction of ferrate(VI) concentration indirectly correlates the decomplexation/degradation of metal(II)-complexed species. Therefore, the change in ferrate(VI) concentration as a function of time for different metal(II)-complex species concentrations are calculated from the absorbance data recorded at 510 nm wavelength and at different pH values i.e., pH 8.0, 9.0 and 10.0. The results obtained e.g., at pH 8.0 are presented in Figs. 1, 2 and 3, respectively for copper(II)-NTA and copper(II)-EDTA and cadmium(II)-EDTA systems. The results indicate that, in presence of metal(II)-complex species, with the lapse of time the ferrate(VI) is decomposed gradually and attains almost a constant value within Ca 14 min of contact. Moreover, this decrease in ferrate(VI) concentration is highly dependent to the solution pH, reaction time and concentrations of complex species in solution . This is demonstrated with the fact that ferrate(VI) is found to be degraded rapidly in presence of metal(II)-complex species during the initial period of contact. Quantitatively, within initial 10 min, the ferrate(VI) removal is 20% to 40% for various molar concentrations of metal(II)-complex species at pH 8.0. This fast initial reduction of ferrate(VI) is in general increased with decreasing the solution pH from 10.0 to 8.0. This is explicable with the fact that the redox potential of ferrate(VI) is significantly high at lower pH values (2.20 V and 0.72 V at pH 1 and pH 14, respectively) which enables ferrate(VI) to decomplex/or degrade the complex species from aqueous solutions [25, 26]. It is further observed that increasing the molar concentration of Cu(II)-NTA, Cu(II)-EDTA or Cd(II)-EDTA, in general, was caused to enhance the decomplexation/degradation of these complexed species in solutions since more and more ferrate(VI) is reduced with an increased rate. Increasing the concentration of copper(II)-NTA from 0.5 mmol/L to 15.0 mmol/L, the corresponding percent reduction of ferrate(VI) is increased from 11.0% to 43.5% within 20 min of contact at pH 8.0. Similarly, the copper(II)-EDTA and cadmium(II)-EDTA systems, the similar increase was recorded from 5.0% to 25.6% and 14.6% to 41.6%, respectively at pH 8.0. The increase in reduction of ferrate(VI) with increase in pollutant concentrations is again pronounced at lower pH values. This again indicates that the acidic conditions favors greatly the decomplexation of metal(II)-complex species in presence of ferrate(VI). Several reports for other metal organo-complex systems indicate somewhat similar findings [35, 40].

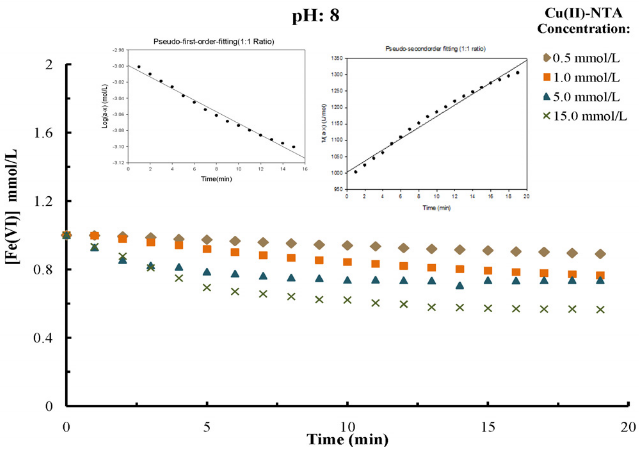

Fig. 1. Degradation of NTA by ferrate(VI) as a function of time for different concentrations of Cu(II)-NTA at constant pH: 8.0 [Initial [Ferrate(VI)]: 1.0 mmol/L].

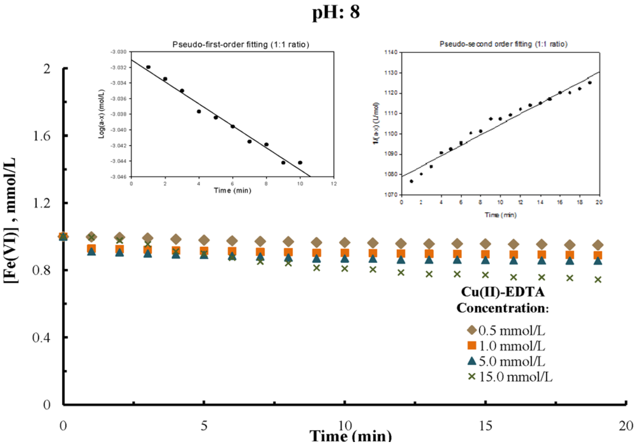

Fig. 2. Degradation of EDTA by ferrate(VI) as a function of time for different concentrations of Cu(II)-EDTA at constant pH: 8.0 [Initial [Ferrate(VI)]: 1.0 mmol/L].

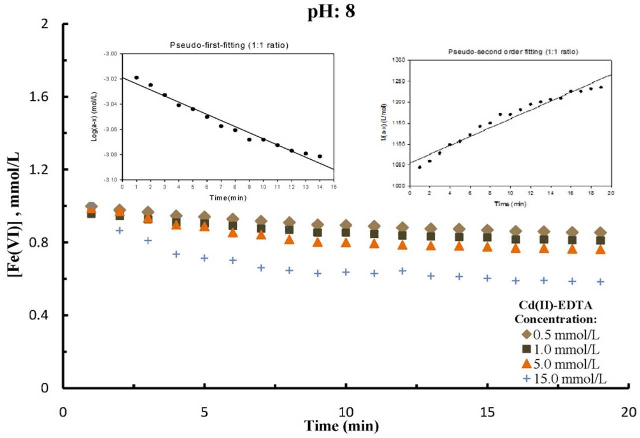

Fig. 3. Degradation of EDTA by ferrate(VI) as a function of time for different concentrations of Cd(II)-EDTA at constant pH: 8.0 [Initial [Ferrate(VI)]: 1.0 mmol/L].

3.1.2. Kinetics of metal(II)-complex decomplexation/degradation

The reduction kinetics of ferrate(VI) in presence of various concentrations of copper(II)-NTA, copper(II)-EDTA or cadmium(II)-EDTA at different pH values and at varied molar ratios (i.e., pollutant to Fe(VI) ratios) were carried out utilizing the time dependence absorbance/or ferrate(VI) concentration data collected at different pH values and molar ratios of ferrate(VI) to metal(II)-complex species. It was demonstrated previously that the reduction of potassium ferrate(VI) into iron(III) as in the form of ferric(III) hydroxide was occurred with the below mentioned reductive pathways [40, 43]:

$$2FeO_4^{2-} + 3H_2O \rightarrow 2Fe(OH)_3 + 5[O] + 4e^- \tag{1}$$

$$[O] + H_2O \rightarrow 2 \cdot OH \tag{2}$$

$$2 \cdot OH \rightarrow H_2O_2 \tag{3}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4}$$

The hydroxyl free radical generated is one of strong oxidizing agent [44] which is readily decomplex/degrade the pollutants from aqueous solutions. The simple kinetics of the degradation of copper(II)-NTA, copper(II)-EDTA or cadmium(II)-EDTA is then discussed. The basic equation for reduction of ferrate(VI) could be represented as:

$$K_2Fe^{VI}O_4 + Metal(II)\text{ - }complex \rightarrow Fe(OH)_3 + Oxidized\,By\text{ - }products + CO_2 + NOX \tag{5}$$

It was assumed that ferrate(VI) caused, partly/or fully, to mineralize the NTA/or EDTA to its end products, which was analyzed by the TOC values. The rate of decomposition of ferrate(VI) is simply expressed as:

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)]^m[Metal(II) - complex]^n \tag{6}$$

$$-\frac{d[Fe(VI)]}{dt} = k_1 \times [Fe(VI)]^m \tag{7}$$

where,

$$k_1 = k[Metal(II) - complex]^n \tag{8}$$

The time dependence change in ferrate(VI) concentration is further utilized to simulate in the Eq. (7) to optimize the value of m=1 or 2 i.e., to employ the pseudo-first and pseudo-second order rate equations. Results are presented graphically in figs. 1, 2 and 3 (as in insets), respectively for copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA systems (e.g., at pH 8.0 having 1:1 molar ratio of metal(II)-complex and ferrate(VI)). The estimated rate constant values along with the R^2 values both for the pseudo-first and pseudo-second-order rate equations were returned in Table 1, 2 and 3, respectively for the copper(II)-NTA, cop-

Table 1. Pseudo-first and Pseudo-second Order Rate Constants Obtained for the Reduction of Ferrate(VI) Using Various Concentrations of Cu(II)-NTA at Different pH Conditions

[Cu(II)-NTA] (mmol/L)	Pseudo-first order rate constant ($\times 10^{-2}$) (1/min)						Pseudo-second order rate constant (L/(mol·min))					
	pH 8.0		pH 9.0		pH 10.0		pH 8.0		pH 9.0		pH 10.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.5	0.69	0.997	0.60	0.999	0.41	0.874	6.87	0.998	6.28	0.999	4.37	0.893
1.0	1.66	0.986	0.64	0.999	0.55	0.992	17.10	0.985	6.91	0.999	6.10	0.991
5.0	2.97	0.900	2.26	0.959	0.83	0.992	19.12	0.872	11.66	0.721	68.83	0.956
15.0	6.96	0.990	4.72	0.930	1.64	0.958	36.57	0.966	17.06	0.575	16.41	0.960

Table 2. Pseudo-first and Pseudo-second Order Rate Constants Obtained for the Reduction of Ferrate(VI) Using Various Concentrations of Cu(II)-EDTA at Different pH Conditions

[Cu(II)-EDTA] (mmol/L)	Pseudo-first order rate constant ($\times 10^{-2}$) (1/min)						Pseudo-second order rate constant (L/(mol·min))					
	pH 8.0		pH 9.0		pH 10.0		pH 8.0		pH 9.0		pH 10.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.5	0.28	0.930	0.18	0.990	0.05	0.889	2.77	0.933	1.76	0.977	4.09	0.889
1.0	0.32	0.981	0.41	0.933	0.16	0.952	3.73	0.986	4.26	0.937	1.62	0.981
5.0	0.51	0.982	1.08	0.978	0.44	0.952	4.10	0.935	14.06	0.984	4.69	0.986
15.0	3.45	0.984	2.10	0.984	2.03	0.904	27.80	0.988	15.32	0.960	6.12	0.902

Table 3. Pseudo-first and Pseudo-second Order Rate Constants Obtained for the Reduction of Ferrate(VI) Using Various Concentrations of Cd(II)-EDTA at Different pH Conditions

[Cd(II)-EDTA] (mmol/L)	Pseudo-first order rate constant ($\times 10^{-2}$) (1/min)						Pseudo-second order rate constant (L/(mol·min))					
	pH 8.0		pH 9.0		pH 10.0		pH 8.0		pH 9.0		pH 10.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.5	0.69	0.947	0.23	0.977	0.14	0.990	9.08	0.960	2.52	0.987	1.62	0.992
1.0	0.92	0.973	0.23	0.987	0.23	0.991	12.62	0.978	2.93	0.979	2.68	0.990
5.0	1.84	0.940	0.46	0.955	0.35	0.988	16.28	0.890	5.66	0.985	3.80	0.988
15.0	6.22	0.920	1.84	0.986	1.45	0.988	32.47	0.830	14.59	0.935	80.92	0.990

per(II)-EDTA and cadmium(II)-EDTA systems studied at varied molar ratios and at different pH values. Results showed that the rate constant was decreased significantly with the increase in pH from 8.0 to 10.0; clearly indicated the rate of reduction of ferrate(VI) or the degradation of M(II)-complex species was more pronounced at lower pH values.

Quantitatively, it is observed that increasing the pH from 8.0 to 10.0, the rate constant value is decreased, respectively from 1.66×10^{-2} to 0.55×10^{-2} min^{-1} (for pseudo-first-order) and from 17.10 to 6.10 L/(mol·min) (for pseudo-second-order) at 1:1 molar ratios of ferrate(VI) and copper(II)-NTA system. Similarly, for copper(II)-EDTA system increasing the pH from 8.0 to 10.0 the rate constant is decreased, respectively from 0.32×10^{-2} to 0.16×10^{-2} min^{-1} (for pseudo-first-order) and from 3.73 to 1.62 L/(mol·min) (for pseudo-second-order) at the 1:1 molar ratio of ferrate(VI) to copper(II)-EDTA. Moreover, in case of cadmium(II)-EDTA system, the rate constant is decreased from 0.92×10^{-2} to 0.23×10^{-2} min^{-1} (for pseudo-first-order) and from 12.62 to 2.68 L/mol/min (for pseudo-second-order) for the similar increase in pH, respectively from pH 8.0 to 10.0 at the 1:1 molar ratio of ferrate(VI) and cadmium(II)-EDTA. Interesting to note that the reduction of ferrate(VI) is quite insignificant or not much pronounced for copper(II)-EDTA system which indicates the relative stability of copper(II)-EDTA chelate (stability constant value = $10^{18.80}$) [45]. This apparently hinders the rate of reduction of ferrate(VI). It was reported previously that the degradation of EDTA and NTA in natural conditions proceeded with the growth of specific bacteria from the subclass of *Procteobacteria*. Further, reported that the metal(II)-EDTA complexes with the stability constants below 10^{12} such as Ba(II), Mg(II), Ca(II) and Mn(II) were degraded efficiently whereas chelates with higher stability constants such as Fe(III),Co(II), Cd(II), Pb(II), Ni(II) or Cu(II) were not metabolized [46]. It was also observed that the rate of reduction of ferrate(VI) was significantly higher at lower pH values, this is because of an enhanced reactivity of ferrate(VI) at lower pH values [26, 27]. These results are in a line with the other studies conducted for the decomposition of other complex species by ferrate(VI) [40].

Further, the overall rate constant 'k' (Eq. (6)) is estimated using Eq. (8). The k_1 values obtained at different concentrations of [Metal(II)-complex] is plotted against the concentration of metal(II)-complex both for pseudo-first-order and pseudo-second order rate constant values. Additionally, the value of 'n' is also optimized with its probable values of 1 and 2; but the data is best fitted for the m=1 and for n=1 as relatively higher value of R^2 is obtained for these systems at various pH conditions (*cf* Figs. 4, 5 and 6, respectively for the copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA systems at pH 9.0). Employing these plots obtained separately at different pH i.e., 8.0, 9.0 and 10.0 are utilized to deduce the overall rate constant values (k) using the slope of these lines. The values of k along with R^2 values are then returned in Table 4. In general, increasing the pH from 8.0 to 10.0, the overall rate constant values are decreased. As pH is increased from 8.0 to 10.0, the overall rate constant is found to be decreased from 4.8 to 1.2 L/(mol·min) for copper(II)-NTA system. Whereas the increase in pH from 8.0 to 9.0 the overall rate constant k is decreased from 2.2 to 1.3 for copper(II)-EDTA and from 4.1 to 0.9 L/(mol·min) for cadmium(II)-EDTA systems, respectively. The decrease in rate constant values at higher pH values is ascribed due to the fact that the reactivity of ferrate(VI) is increased at lower pH values. The speciation studies conducted elsewhere showed that at around pH 8.0 the protonated species of the ferrate(VI) i.e., $HFeO_4^-$ was gradually increased (i.e., *Ca*. 50% at pH 8.0) since the pk_a value for the acid dissociation of $HFeO_4^-$ was reported to be 7.3 [34]:

$$HFeO_4^- \leftrightarrow FeO_4^{2-} \qquad (pk_a = 7.3) \tag{9}$$

Since the protonated species $HFeO_4^-$ were possessed with larger spin density hence, the reactivity of protonated species increased significantly [47, 48]. Moreover, the alkyl groups are found to be electron releasing groups, hence enhances the reactivity of protonated species $HFeO_4^-$ in aqueous solutions [32]. Similarly, the higher degradation was reported with the protonated species of ferrate ($HFeO_4^-$) than the deprotonated species (FeO_4^{2-}) in the degradation of various steroid estrogen including BPA from aqueous solutions [49].

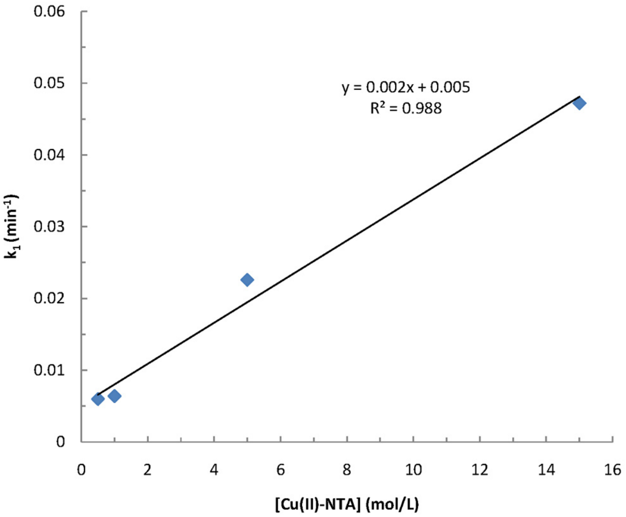

Fig. 4. Fitting of pseudo-first-order rate constant values for the degradation of ferrate(VI) as a function of Cu(II)-NTA concentrations at pH 9.0.

Table 4. Overall Rate Constant in the Decomplexation/Degradation of Metal(II)-complex by Ferrate(VI) at Different pH Conditions

pH	Cu(II)-NTA system		Cu(II)-EDTA system		Cd(II)-EDTA system	
	k (L/(mol·min))	R^2	k (L/(mol·min))	R^2	k (L/(mol·min))	R^2
8.0	4.8	0.913	2.2	0.940	4.1	0.973
9.0	2.9	0.988	1.5	0.906	1.2	0.965
10.0	1.2	0.842	1.3	0.979	0.9	0.958

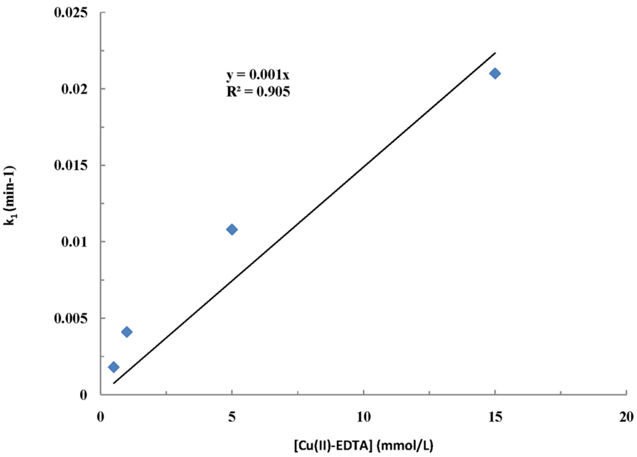

Fig. 5. Fitting of pseudo-first-order rate constant values for the degradation of ferrate(VI) as a function of Cu(II)-EDTA concentrations at pH 9.0.

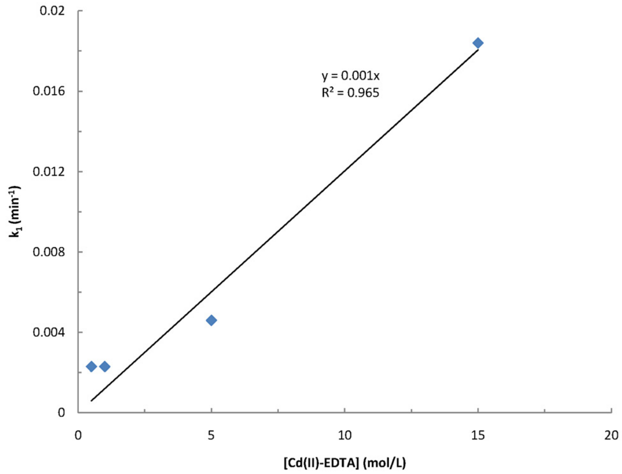

Fig. 6. Fitting of pseudo-first-order rate constant values for the degradation of ferrate(VI) as a function of Cd(II)-EDTA concentrations at pH 9.0.

It is also noted that 1:1 stoichiometry prevailed in decomplexation/degradation of metal(II)-complex with ferrate(VI) at various pH values. Previously, it was indicated that the oxidation of thiocyanate with ferrate(VI) followed pseudo-first-order rate kinetics with respect to the ferrate(VI) concentration. Therefore, the rate constant (k_1) at various concentrations of thiocyanate was evaluated [50]. Further, the plot between k_1 versus [SCN^-] was found to be linear, suggesting that the rate law followed first order with respect to both the reactants i.e., ferrate(VI) and SCN^-. The rate of reaction was increased with decreasing the pH. This inferred that protonation of ferrate(VI) caused to enhance the reactivity of ferrate(VI). Similar results were also reported for the decomposition of copper(I)-cyanide complex systems [51]. A recent report also indicated that the copper(II)-IDA and zinc(II)-IDA followed the first-order rate kinetics for both reactants i.e., ferrate(VI) and metal(II)-IDA and the overall rate constant values were greatly decreased with increasing the solution pH from 8.0 to 10.0 [40].

3.2. Mineralization of NTA/or EDTA

Oxidation of decomplexed or free NTA/or EDTA by ferrate(VI) is assessed by the TOC measurements. The total organic carbon data are obtained for various stoichiometric ratios of ferrate(VI) and metal(II)-complex (1.0:0.5 to 1.0:15.0) treated at different pH conditions i.e., pH 8.0 to 12.0. Results are shown graphically in Figs. 7, 8 and 9, respectively for the copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA systems. The results show that NTA/or EDTA is effectively degraded/mineralized by ferrate(VI) at least at lower pH 8.0 and lower metal(II)-complex concentrations. At higher concentrations of metal(II)-complex and at higher pH values i.e., pH 12.0 the percent TOC of NTA or EDTA is significantly decreased. This demonstrates that ferrate(VI) is able to oxidize NTA/or EDTA more effectively at lower concentrations of the metal(II)-complex. More quantitatively, increasing the pH from 8.0 to 12.0, the percent TOC removal was decreased from 25.32% to 17.33% (for copper(II)-NTA), from 64.55% to 32.11% (for copper(II)-EDTA) and from 24.21% to 18.80% (for cadmium(II)-EDTA), respectively for the 1:1 molar ratios of ferrate(VI) and metal(II)-complex species. The results again inferred that the ferrate(VI) is relatively more reactive at lower pH values i.e., at pH 8.0 comparing to higher pH values i.e., at pH 12.0. These results are in a line to the kinetic data obtained by the UV-vis measurements where it was noted that an increase in metal(II)-complex concentration invariably caused to increase the degradation rate of ferrate(VI). Previously, it was reported that an increase in pollutant concentration caused to increase the degradation rate of ferrate(VI) however, the percent removal of TOC was found to be less and an enhanced level of intermediates were, perhaps, formed [42, 52]. Naphthalene and trichloroethylene were mineralized almost completely by the ferrate(VI) [53]. Similarly, increasing the ferrate(VI) dose in the treatment of bisphenol A (BPA) (ferrate(VI):BPA ratio) the value of DOC (dissolved organic carbon) was decreased from 60% to 20%. It was also reported that the degree of degradation and mineralization for ferrate(VI):BPA

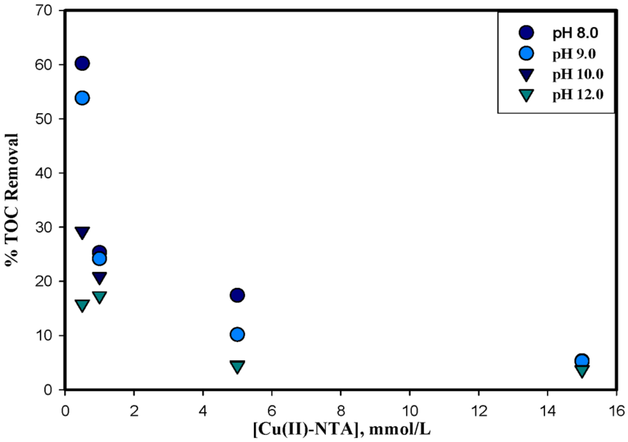

Fig. 7. Degradation of NTA for different concentrations of Cu(II)-NTA treated with ferrate(VI) at different pH values [Initial [Ferrate(VI)] :1.0 mmol/L].

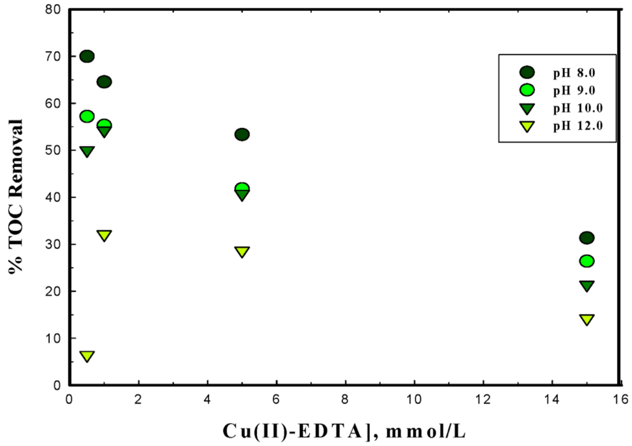

Fig. 8. Degradation of EDTA for different concentrations of Cu(II)-EDTA treated with ferrate(VI) at different pH values [Initial [Ferrate(VI)] :1.0 mmol/L].

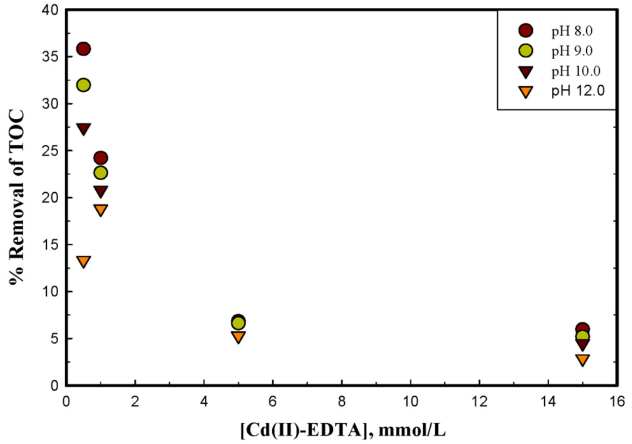

Fig. 9. Degradation of EDTA for different concentrations of Cd(II)-EDTA treated with ferrate(VI) at different pH values [Initial [Ferrate(VI)] :1.0 mmol/L].

ratios was obtained to be greater than 1, hence, it indicated that some intermediates of BPA was formed but with the time, the intermediates were also mineralized [42].

3.3. Simultaneous Removal of Copper(II)/or Cadmium(II)

The reduced ferrate(VI) into iron(III)hydroxide is an useful coagulant or the presence of $Fe(OH)_3$ is even an excellent adsorbent for heavy metal toxic ions hence, ferrate(VI) may serve as multifunctional use in such wastewater treatment strategies. Therefore, in order to assess the suitability of ferrate(VI) in simultaneous removal of copper(II)/or cadmium(II) from the ferrate(VI) treated samples is further investigated. The ferrate(VI) treated samples are filtered and part of this sample is subjected to increase the solution pH 12.0 by the drop wise addition of concentrated NaOH and again filtered. Thereafter, both the samples are subjected to the total bulk copper(II) or cadmium(II) concentrations using AAS. The percent removal of copper(II) or cadmium(II) by the ferrate(VI)

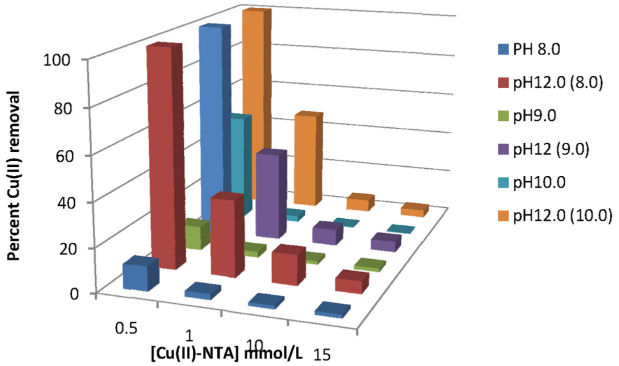

Fig. 10. Simultaneous removal of Cu(II) for different concentrations of Cu(II)-NTA treated with Ferrate(VI): 1.0 mmol/L at different pH values.

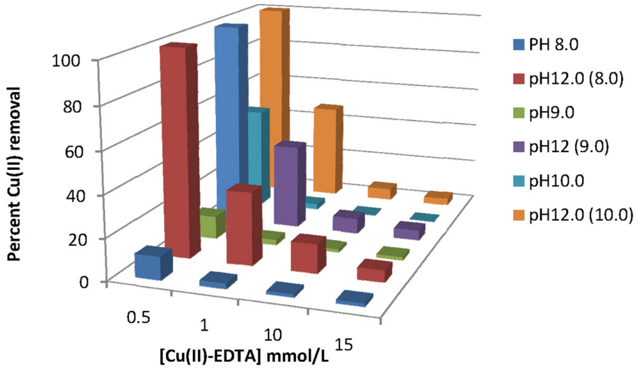

Fig. 11. Simultaneous removal of Cu(II) for different concentrations of Cu(II)-EDTA treated with Ferrate(VI): 1.0 mmol/L at different pH values.

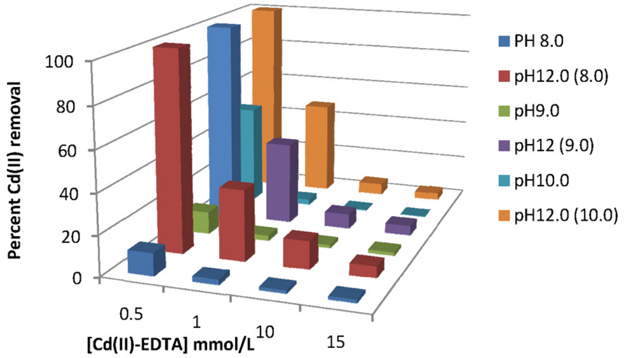

Fig. 12. Simultaneous removal of Cd(II) for different concentrations of Cd(II)-EDTA treated with Ferrate(VI): 1.0 mmol/L at different pH values.

dose is presented graphically in Figs. 10, 11 and 12, respectively for the copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA systems. The data pertained with these figures clearly indicated that relatively less percent removal of copper(II) or cadmium(II) was obtained at lower pH values. However, once the treated samples pH was increased to 12.0, a significant increase in percent removal, i.e., almost 100%, of copper(II) or cadmium(II) was achieved at least for the lower concentrations of metal(II)-complex species. It was observed that the elevated pH favored greatly the removal of copper(II) or cadmium(II) from aqueous solutions. The enhancement in metal(II) percent removal by the ferrate(VI) treatment at higher pH values is attributed due to the enhanced coagulation occurred at higher pH values. Previously it was obtained that a complete removal of copper(II) was obtained in case of Cu(II)-cyanide complex with partial removal of Ni(II) from Ni(II)-cyanide complexes [30]. Similarly, Cu(II) and Zn(II) were removed simultaneously when their IDA complexes were treated with ferrate(VI) [40].

4. Conclusions

The higher oxidation state of iron i.e., ferrate(VI) is utilized in the treatment of wastewaters contaminated with metal(II)-complex species (*viz*., copper(II)-NTA; copper(II)-EDTA and cadmium(II)- EDTA). The kinetics of degradation is discussed with the reduction of ferrate(VI) studied at wide range of pH (8.0 to 10.0) and at varied metal(II)-complexed species (0.5 to 15.0 mmol/L) using a constant dose of ferrate(VI) 1.0 mmol/L. The pseudo-first-order and pseudo-second order rate constants are estimated in the reduction of ferrate(VI) which is then utilized to optimize the overall rate constants in the degradation process. The overall rate constant values are, in general, increased with decreasing the pH from 10.0 to 8.0 which indicates the enhanced applicability of ferrate(VI) at relatively lower pH values. Further, the mineralization of organic species i.e., NTA and EDTA is obtained by the change in TOC values of ferrate(VI) treated samples. Results show that the percent TOC values are decreased with increasing the pH and molar ratios of ferrate(VI): metal(II)-complex. The simultaneous removal of metallic impurities i.e., copper(II) or cadmium(II) is obtained at the treated pH and also at the elevated pH i.e., 12.0 as to enhance the coagulation to remove the metals. Almost a complete removal of free copper or cadmium is obtained at pH 12.0 at least at lower stoichiometric ratios and at all studied pH values. Overall, the ferrate(VI) is found to be an useful chemical possesses multifunction application in wastewater treatment as in the first step it oxidizes the degradable impurities and in the second step it removes the non-degradable metallic impurities perhaps by the coagulation process. These results show that ferrate(VI) treatment is effective at least for the treatment of wastewaters contaminated with copper(II)-NTA, copper(II)-EDTA and cadmium(II)-EDTA complex species. Moreover, the treatment process is free from toxic by-products hence to be known as 'Green Treatment'.

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