FERRATE(VI): A GREEN CHEMICAL FOR THE TREATMENT OF AQUEOUS WASTES

A Thesis submitted

in partial fulfilment of the requirements for the Degree of

Doctor of Philosophy
in
Chemistry

By

LALRAMNGHAKI PACHUAU

DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
MIZORAM UNIVERSITY
TANHRIL, AIZAWL- 796004

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Mizoram University

Greater Deeds Remain

(A central University under the Act of Parliament)

Department of Chemistry

School of Physical Sciences

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CERTIFICATE

This is to certify that the thesis entitled, ***'Ferrate (VI): A green chemical for the treatment of aqueous wastes',*** submitted by ***Ms. Lalramnghaki Pachuau,*** for the degree of ***Doctor of*** Philosophy in the Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by her under my supervision. She 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 degree in any other university.

Dated: 5 August, 2013

(DIWAKAR TIWARI)
Supervisor

DECLARATION OF THE CANDIDATE

I, Lalramnghaki Pachuau, a Ph.D. Scholar in Chemistry Department, Mizoram University, Aizawl, do hereby solemnly declare that the subject matter of this thesis is the record of the work done by me. I have duly worked on my Ph.D. thesis under the supervision of Professor Diwakar Tiwari, Department of Chemistry, Mizoram University, Aizawl. This is being submitted to the Mizoram University for the degree of Doctor of Philosophy in Chemistry and that I have not submitted this work to any other University or Institute for any other degree.

I also declare that the present investigation relates to bonafide research works done by me and the title of the thesis is **'FERRATE(VI): A GREEN CHEMICAL FOR THE TREATMENT OF AQUEOUS WASTES'.**

Dated: 5/8/13

(LALRAMNGHAKI PACHUAU)
Candidate

DEDICATION

I dedicate this thesis to my beloved father, P.C.Lalduha, who had left us and this world on the ninth of May, 2011. This thesis is here today only because of my late father, whose dearest wish had always been for me to fully accomplish my academic pursuit with a Ph.D degree. I remember his joy and enthusiasm when I finally joined Ph.D programme under Mizoram University and also his appreciations and constant encouragements during my research works, although, sadly was not able to see me through to the end of this journey. The desire and the determination to fulfill my father's dream had been the constant source of inspiration for me, giving me the strengths to overcome difficulties and hardships in my research endeavor, to finally present this thesis. I thank God for blessing me with such a loving, inspiring father who had taught me the values of life and hard works. My deepest sorrow and only regret this day is that he did not live to see me with this thesis, and my greatest joy is to be able to finally accomplishing his wish! Although he is no longer of this world, his loving memories will continue to be the guiding star in my life for the days to come.

'So, with this thesis, dear father, I thank you with all my heart and you will always be lovingly remembered with smiles and tears. We love you'

Lalramnghaki Pachuau

Acknowledgements

Foremost, I sincerely express my heartfelt gratitude to my Research Supervisor, *Prof. Diwakar Tiwari*, Department of Chemistry, Mizoram University, for his active guidance throughout my research work. The depth of his devotion, truthfulness and grand passion for his works, I will not cease to admire and will remain the source of my inspirations today and for the days to come. I thank him, particularly for his patience with me. I am most fortunate to have such an expertise and efficient supervisor, I could not think of a better advisor or mentor for my pH.D study, thanks to my dear friend-

Dr Rosy Lalnunsangi for introducing me to him, and for her continued care and support during my research days till date.

I express my sense of gratitude to *Er. Dunglena*, former Chairman, *Pu R.C. Thanga* (I.F.S. Rtd), Chairman and *Er. C. Lalduhawma*, Member Secretary, Mizoram Pollution Control Board for allowing me to pursue Ph.D programme and for their understanding and support of my work.

I was able to complete my analytical work with the valuable help I received from some of the persons and institutions to whom I would like to convey my gratitude herewith:

To the Mizoram Pollution Control Board for the use of their laboratory and the facilities available therewith.

To the Public Health Engineering Department, Govt. of Mizoram for the use of their laboratory. My heartfelt gratitude goes to *Mr. P.C. Biakmawia*, Chief Chemist for permitting me to use their sophisticated AAS instrument and to his staff, *Ms. Vanlalhruaii* and *Mr. P.H. Vanlalawmpuia* for their kind assistance with the handling of the instrument.

To *Prof. Seung Mok Lee* and his team, Deptt. of Environmental Engineering, Kwandong University, Gangnung, Korea; To *Prof. J.K. Yang*, Division of General Education, Kwangwoon University, Seoul, for parts of my research works were undertaken under their institutions with their kind support.

My special gratitude is extended to my fellow Research Scholar, Mr. Lalsaimawia Sailo, for all his valuable inputs in collection and analysis of data. My data would be incomplete without his contributions.

I also convey my sincere thanks to Dr. Muthukumaran, R., Head of the Chemistry department, MZU for making it possible for me to carry out my Ph.D activities in the Chemistry department, MZU and to other faculty members of the Department, *viz., Dr. Zodinpuia Pachuau, Dr. N. Mohandas Singh, Dr. Rajkumar Mishra, Dr. Ved Prakash Singh*, for their encouragement and support.

I am happy to acknowledge the support and encouragement I received from all my fellow research scholars in the department of Chemistry, *v.i.z., Dr C. Laldawngliana* (now awarded Ph.D degree), *Mr. Lalhmunsiama, Mr. Thanhmingliana, Mr. C.Lalhriatpuia, Miss Lalthlengliani, Miss Lalchhingpuii* and others. I am particularly indebted to *Miss Lalthuammawii* and *Mr. John Vanlalhruaia* for their endless help and support.

I really appreciate the hospitality and care extended to me by *Mrs. Alka Tiwari* and *Adity Tiwari* at all times. Their warm faces and kind words of encouragement, I will never forget.

The constant love and care, my lovely family have bestowed upon me makes it possible for me to accomplish my research work. I feel particularly very lucky to have my beloved sister, *Laledenthari* always beside me during preparation of my research report. Her computer knowledge is a blessing for me.

I have been blessed with wonderful friends who are there for me always-

Dr Lalthlamuana Pachuau, Ronen L. Guite, Joseph Lalhmunliana, Dandy Lalduhawmi, Lalmuanpuia and Rosangtuali. I thank them for standing besides me through thick and thin.

Last, but not the least, I would like to acknowledge my colleagues and friends at Mizoram Pollution Control Board – *Miss P.C. Lalmuanpuii, Mrs. Lalngaihsaki Sailo, Mrs. Lalnunziri, Mrs. B.Laldikzuali, Miss Lucy Ngurkhumi Sailo, Mr. Alfred Malsawmsanga Chenkual, Mr. Lalremsiama Varte* and others for being always so supportive of me.

All this possible, because our Heavenly Father has been blessing me with health and loving family. I thank Him for His countless blessings and guidance throughout my life, enabling me fulfilling my father's dreams.

Lalramnghaki Pachuau

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CHAPTER 1

Introduction

1. INTRODUCTION

Aqueous wastes or wastewaters were defined as a combination of the liquid or water-carried wastes removed from residences, institutions, and commercial and industrial establishments, together with groundwater, surface water and storm water as may be present (Cerra and Maisel, 1972).

Freshwater crisis has become one of the major global environmental concerns. The earth's reserve of water, estimated at approximately 1.4 billion cu km, may seem enormous. However, practically 97.5 percent of these reserves are saline, not suitable for consumption and that only *Ca*. 2.5 percent of all the reserves constitute freshwater component and two-thirds of this is frozen in glaciers, mainly in the Arctic and Antartic regions. Hence, there is only 10.5 million cu km of liquid fresh water on this globe (Novitsky and Khamizov, 2002). Therefore, the freshwater resources are under extreme stress due to over consumption/ exploitation with increasing demand of water in various sectors of human activities. Further, due to climate change, rapid rise in urbanization and industrial and agricultural activities, water resources are exceedingly polluted through haphazard continuous discharge of various forms of wastes. The amount of waste disposed in water reservoirs around the world increased manifolds over the last few decades. Statistical data on ocean pollution reveals that every year 14 billion pounds of waste is disposed in the oceans all over the world. According to the data compiled by the World Water Assessment Program (WWAP), 2 million tons of human waste is disposed in water bodies every single day. Over the last two or three decades, the tremendous rate of increase in pollution load resulted in the degradation of water quality around the globe limiting the access of fresh or clean water. According to the World Bank and World Health Organization, 2 billion people lack in access of fresh/clean water and 1 billion people do not have enough to even meet their daily needs and every year millions die due to preventable water-related diseases. Therefore, the situation becomes alarming and availability of fresh water is an issue of concern around the globe.

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). 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. HEAVY METAL POLLUTANTS IN AQUEOUS WASTE

The ever growing industrial uses of heavy metals led to the steady increase in the concentration of the toxic metal ions in the global aquatic environment. The contamination of surface/ground waters by heavy metal toxic ions is a serious environmental and public concern because of the fact that these ions are virtually non-biodegradable and tend to accumulate within the bio-system, causing various biological disorders (Martin, 1986). Besides the toxic and harmful effects to the aquatic life, the extended perseverance of these pollutants in the biological systems and accumulation in the biosphere through the food chain results in environmental and occupational hazards. Contamination of water bodies with heavy metals arises mainly from the aqueous waste streams of industries *viz.*, metal plating, mining operations, tanneries etc. Toxic metals, such as mercury, cadmium, arsenic, copper and many other species tend to accumulate with the sediments from which they tend to release by various processes of remobilization which further can move up to the biological chain, thereby reaching human beings where they produce chronic and acute ailments (Förstner *et* *al.*, 1981). Several heavy metals are reported to be essential at trace level concentration, however, an increased level of intake caused adverse effects to the living beings. Heavy metals, such as cadmium (Cd), copper (Cu), zinc (Zn), nickel(Ni) etc. often present in industrial waste/effluent waters are possessed with potential health hazards. The toxicities of these heavy metal toxic ions are highlighted in the sections included below.

1.1.1. Cadmium

Cadmium, next to mercury is the most notorious among the heavy metal pollutants. It is one of the non-essential elements; therefore, the presence of cadmium in the environment can only cause harmful effects. It is often associated with zinc, generally at levels around 0.5% of the zinc levels. In natural unpolluted freshwaters the cadmium levels vary from 0.01 ppb to 0.4 ppb levels (Hart, 1984). For use of drinking water, it is recommended by national and international regulatory agencies that the total cadmium concentration should not exceed the maximum of 0.01 ppm in raw water supply (WHO, 1971; USEPA, 1980a; ISI, 1982). A maximum concentration of 2.0 ppm is recommended for the discharge of cadmium containing effluents on inland surface waters by Indian Standard Institutions (1981).

Sources:

The sources responsible for cadmium contamination are mainly of anthropogenic origin. According to an estimate, approximately 500 tons of cadmium enters into the environment annually because of natural weathering only and about 2000 tons is released annually as a result of human activities. About 20% of released cadmium comes from zinc mining and smelting operations with another 30% from the manufacture, use and disposal of cadmium products. The remaining 50% is dispersed as contaminants in other substances including phosphate fertilizers, sewage effluents and sludges (Abbasi *et al.*, 1998). Cadmium is mainly used in industries, such as metal plating, smelting, paint pigments, batteries, fertilizers, metallurgical alloying, mining, ceramics and other industrial operations etc. (Davis *et al.*, 2000; Iqbal and Edyvean, 2005).

Toxicity:

In general, cadmium is recognized only because of its acute and potential toxicity, but after the incident of "*itai-itai*" or ouch-ouch bone degenerative disease in Japan in late 1940's due to cadmium poisoning (Aoshima *et al.*,2003; Kasuya, 2000; Hutton, 1983), the concerns of cadmium toxicity received a greater interest. Cadmium is extremely toxic to aquatic organisms, even at very low concentration. 70 percent reduction in photosynthesis of *Chlorella pyrenoidosa* at 0.1 ppm was reported, and in *Chlorella vulgaris*, the corresponding effect was observed at 1.0 ppm (Burnison *et al., 1975)*. The acute toxicity of cadmium to freshwater invertebrates was seen widely; the acute toxic concentration of cadmium to invertebrates varies from 0.005 to 520 ppm (Abbasi *et al*., 1998). The lethal concentration of cadmium for four stages of rainbow trout was reported to vary within the range of 0.001 to > 0.027 ppm (Chapman, 1978).

Cadmium is highly toxic to human as well. It is biologically very active; therefore gives rise to both acute and chronic poisoning. Ingestion of large amounts of cadmium (e.g., 13 to 15 µg/g Cd) leads to nausea, diarrhea, abdominal pains, muscular rheumatism and weaknesses (USEPA, 1980a). Cadmium toxicity was observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects (Hajialigol *et al.*, 2006). Cadmium was found to be carcinogenic and caused for lung fibrosis and dyspnea (Sud *et al.*, 2008). Chronic exposure to elevated levels of cadmium caused for bone degeneration, liver damage etc. (Iqbal *et al.*, 2007). Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache sometimes referred as 'the cadmium blues'. More severe exposures can cause tracheal bronchitis, pneumonitis and pulmonary edema. Symptoms of inflammation may start hours after the exposure and include cough, dryness and irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain. Cigarettes are additional source of cadmium exposure. Although there is generally less cadmium in tobacco than in food, but lungs absorb cadmium more efficiently than the stomach (Jarup, 1998). Workers exposed to cadmium-containing fumes were reported to develop acute respiratory distress syndromes (ARDS) (Barbee and Prince, 1999). Intake of cadmium-contaminated food caused acute gastro-intestinal effects, such as vomiting and diarrhoea (Nordberg, 2004). The IARC (International Agency for Research on Cancer) decided to classify cadmium as one of human carcinogen group I. Latest data, however supported the assumption that only an uptake of cadmium via the respiratory system leads to carcinogenic potentials(Jin *et al.*, 2002).

1.1.2. Copper

Copper is the first metal harnessed by man. Copper and its alloy (Brass) are widely utilized by man throughout the history of human civilization. Copper is one of the essential trace element required by humans and living organisms. It is one of the essential components of many metalloenzymes and respiratory pigments; the concentration of copper in human is estimated to be 75 to 150 mg (NAS, 1977). In unpolluted waters, copper concentrations were estimated at 0.0006 to 0.4 ppm with a median value of 0.01 ppm (Bowen, 1966). Maximum permissible limit of Copper in drinking water is 0.1 ppm as per Indian Standard Institution (ISI, 1982) and United States Environmental Protection Agency (USEPA, 1980b) and as per the World Health Organization (WHO, 1971), the limit is prescribed as 1.5 ppm. The recommended limit of copper; discharging the industrial effluents on inland surface waters is 3.0 ppm (ISI, 1981).

Sources:

There are several sources of copper emission to the atmosphere. Nriagu (1979a & 1979b) estimated that the total copper emissions in the atmosphere amounted to 74500 tonnes/year of which 25% were from natural sources like windblown dusts, vegetation exudates, volcanic emissions, sea salt sprays and the rest from anthropogenic sources including metal production, wood and fossil fuel combustion, and waste incineration. Copper reaches the aquatic environment through wet or dry deposition, mining activities, and land runoff, industrial, domestic and agricultural waste disposal. Industrial sources of copper include copper plating, metal pickling baths, pulp and paper mills, metal works, mine water, acid mine drainage etc. Galloway (1972) estimated that about 42000 tons/year of copper are released into the environment through sewage.

Toxicity:

Copper in water is exceedingly toxic to aquatic biota. Several studies indicated that copper causes significant effect on growth, photosynthesis and oxygen evolution in algae species at concentration range of 0.0005 ppm to 63.5 ppm (Abbasi *et al.*,1998*).* Nriagu (1979c) studied and observed that the acute toxicity of copper for several species of aquatic invertebrates varies from 0.0005 ppm to 64.0 ppm.

In human beings, the acute and chronic manifestations of copper poisoning are dependent to the mode of contact and the surroundings in which this contact occurs. An allergic contact dermatitis may result from direct exposure to copper salts or dust. Higher concentrations of copper in the biological systems possessed with several toxic effects (Benaissa and Elouchdi, 2007). Copper can cause severe mucosal irritation and corrosion, widespread capillary damage, central nervous system irritation, stomach and intestinal distress, liver and kidney damage, and anemia (Gardea-Torresdey *et al*.,1996; Ajmal *et al.*, 1998). Human body has a natural mechanism for maintaining the proper level of copper. However, children less than one year old do not show such mechanism, therefore, are more vulnerable to the toxic effects of copper. People with Wilson's disease also showed a problem with maintaining the proper balance and taking care to limit the exposure of copper. Concentration of copper in drinking water with level of 5 to 8 mg/L make the water undrinkable (HDR Engineering Inc, 2001). The incidence of development of green hair after exposure to copper-contaminated water was also recorded (Cooper and Goodman, 1975).

1.1.3. Zinc

Zinc is amongst the ubiquitous elements with its mean concentration in the earth's crust estimated as 70 ppm. In natural freshwaters, such as unpolluted springs, streams, rivers and lakes, zinc concentration rarely exceed 0.5 ppm. (Abbasi *et al.*, 1998). Indian Standards Institute, India (ISI,1981) prescribed a maximum concentration of 5.0 ppm zinc for discharge of industrial effluents on inland surface waters. USEPA (1980c) has recommended 0.117 ppm zinc as maximum continuous concentration for freshwater quality.

Sources:

The sources of zinc pollution are natural as well as anthropogenic. Anthropogenic sources contribute an estimated 414,000 tons of zinc per annum which include primary zinc production, wood combustion, waste incineration, iron and steel production, other atmospheric emissions and municipal wastewaters. Industrial effluents and municipal wastewaters are the biggest sources of zinc pollution. The industrial uses of zinc comprises of zinc coating, electro galvanizing, spraying, painting, zinc alloys, brass, rolled sheets and strips, dry batteries, roofing and exterior fittings on buildings and printing processes are additional sources of zinc contaminating the aquatic environment.

Toxicity:

The toxicity of zinc to freshwater aquatic organisms vary widely within various species of aquatic life (Abbasi,1989; Moore and Ramamoorthy,1984) depending on various biological factors and physico-chemical factors. Zinc concentration between 0.015 ppm to 30 ppm is reported to cause toxic effects in algae (Spear, 1981). Several studies revealed that zinc was found to impair physiological functions of chironomid larvae (Malyarevskaya *et al.*, 1985); stimulate drift of mayfly nymphs (Swain and White, 1985); reduced number of species of chironomidsin British water stream (Armitage and Blackburn, 1985). Zinc is an essential trace element required in the functioning of several enzyme systems and is considered to have low toxicity for humans, however, in concentrations beyond certain limits, it can be highly toxic. The recommended human daily intake of zinc is reported to be within a range of 3.2 to 29.0 mg for various countries (Peereboon, 1985). Perrin and Agarwal (1976) reported a dose of zinc (220-450 ppm) which may produce an emetic effect, and in water the concentration range 675-2280 ppm may produce similar effects. Symptoms of zinc toxicity include vomiting, dehydration, stomach pains, nausea, lethargy, dizziness and muscle incoordination (Sanstead, 1975). The most common sources of zinc poisoning in humans are metal fumes and illness arising from the ingestion of acidic foods prepared in zinc-galvanized containers. Zinc stearates have been found to be possible cause of Pneumonitis. Zinc salts, particularly zinc chloride produce dermatitis upon contact with skin (Sitting, 1976).

1.1.4. Nickel

Nickel is also an ubiquitous elements with an average concentration of 75 ppm in the earth's crust (Levinson, 1974). Nickel concentration in seawater range from 0.1 to 0.5 ppb whereas nickel levels in freshwaters are more variable and range from 0.5 to 600 ppb (Barceloux, 1999). The typical body content of nickel in a normal adult human is approximately 10 mg;

the nickel content of various tissues varies widely (ICRP, 1975). USEPA (1980d) suggested that the maximum concentration of nickel in drinking water should be 0.1 ppm. Normally drinking water contains <0.005 ppm of nickel.

Sources:

Nickel enters the environment through two main pathways; natural such as weathering of minerals and rocks and geothermal emissions, and anthropogenic such as industrial and vehicular emissions. It was estimated by Nriagu and Pacyna (1988) that anthropogenic contribution of nickel to water is ranged between 33 and 194 million kg/year with a median value of 113 million kg Ni/year. Nickel is widely used in industry due to its resistance to corrosion, high strength over a wide temperature range and good alloying properties. It is most extensively used in nickel plating and alloy manufacturing. High nickel alloys are used in chemical, marine, electrical, nuclear and aerospace applications. It is employed as a catalyst in oil refining and other industrial processes.

Toxicity:

Nickel is regarded as one of the essential trace elements for human, plant and animal nutrition, but can also cause widespread toxicity at higher levels. The studies conducted on impact of nickel on algal species and aquatic plants reveal that nickel can inhibit algal growth within concentration range of 0.05 – 0.5 ppm (Stokes *et al.*, 1973; Hutchinson, 1973) and suppress photosynthetic oxygen evolution in aquatic plant *Elodea* by 50% at 723 ppm (Brown and Rattingan, 1979). Numerous animal studies demonstrated significant respiratory toxicity following nickel exposure via inhalation. High exposures of Ni_3S_2 (3.6-7.3 mg Ni/m^3) studied in rat; resulted even death, necrotizing pneumonia, emphysema and chronic inflammations in lungs of rat (Benson *et al.*,1987; Dunnick *et al.*, 1988).

Nickel enters human system through ingestion via food, drinking water and breathing. The lungs and nasal cavity are the primary targets for nickel-induced cancers. While these are the most hazardous respiratory effects of nickel exposure, other respiratory system effects in humans are also reported. Death from adult respiratory distress syndrome occurred in a worker exposed to very high concentrations (382mg/m^3) of metallic nickel (Rendell *et al.*, 1994). Nickel effect on the immune system is twofold. It is a powerful sensitizing agent and, as such, elicits hypersensitivity reactions manifested as contact dermatitis and asthma. In addition, nickel is an immunosuppressant and decreases macrophage and natural killer (NK) cell activity. Nickel Dermatitis was recognized as the most common symptom of industrial exposure of nickel, although high occupational exposures are associated with renal problems and lung cancer (Falk, 1974; Horvath, 1976).

1.2. ORGANIC COMPLEXING AGENTS IN AQUEOUS WASTES

A great deal of evidence exists which suggest that chelating agents, such as aminopolycarbo xylate (APC) and organophosphates(OP) are common water pollutants. Synthetic organic chelating agents such as sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA), and sodium citrate are produced in large quantities for use in metal-plating baths, industrial water treatment, detergent formulations, food preparations etc. These synthetic compounds are commonly discharged to surface water via run offs of sewage treatment plants in a large amount without adequate degradation. This results from the poor efficiency of wastewater treatment plants in removing various classes of organic pollutants like antibiotic and other pharmaceuticals (Zhang *et al.*, 2008; Loganathan *et al.*, 2009; Matamoros *et al.*, 2009). Resulting from the discharge of industrial wastewater effluents from pulp and paper mills, typically individual APCs such as EDTA, NTA or DTPA present in sewage treatment plants and in surface water are characterized by varying concentrations from 10 to 35 mg/L (White and Knowles, 2003) and from 10 to 500 µg of EDTA per liter (Pirkanniemi *et al.*, 2007) respectively, while OP compounds such as Hydroxyethylidene diphosphonic acid (HEDP) and Nitrilotris methylenephosphonic acid (NTMP) are present in the effluents of water treatment plants with their concentrations ranging from 20 to 970µg L^{-1} (Nowack,1997 & 2002).

The increasing use of such chelating organic pollutants in industries as well as domestic purposes cause a global concern because they are not only weakly biodegradable, but also possess high ability to solubilize heavy metals and also enhanced heavy metal transport in the environment. Presently, these are under strict regulatory pressure due to the need for protecting the aquatic environment (Sillanpää, 2005). Although EDTA-chelates are normally non-toxic (Sillanpää *et al.*, 2003), their presence could also affect the underlying groundwater by enhancing the migration of trace metals and radionuclides from contaminated soils or disposal sites to the groundwater (Schmidt and Brauch, 2005). Since chelates, such as ^{60}Co(III)–EDTA could not be effectively adsorbed onto surface minerals, it would facilitate unwanted mobility of the radioactive ^{60}Co in the water bodies (McArdell *et al.*, 1998).In spite of this environmental concern, the consumption of APCs including NTA, EDTA, DTPA and HEDTA in industries increases up to 200000 tons annually worldwide (Nowack and Briesen, 2005), while the consumption of OP attains 60000 tons per year, corresponding to over US$ 2.5 billion in revenue (Nowack and Stone, 2000a&2000b). Due to the production of totally-chlorine free (TCF) pulp, the global consumption of EDTA and DTPA in pulp and paper industries is anticipated to increase over 65000 tons annually (Tucker *et al.*, 1999).

1.2.1. Ethylenediaminetetraacetic acid (EDTA)

Ethylenediaminetetraacetic acid (EDTA) is a powerful chelating agent which is widely used in various industries. The compound was first described in 1935 by Ferdinand Munz who prepared the compound from ethylenediamine and chloroacetic acid (Münz, 1938). It is a powerful complexing agent of metals and a highly stable molecule, offering a considerable versatility in industrial and household uses. The product is marketed worldwide under 30 different trademarks and its use in the world is massive and increasing (Virtapohja and Alén, 1999). Because of its high affinity to metal ions, EDTA is extensively employed in various industries, *viz*., metal plating, nuclear, pharmaceutical, food, photography, pulp/paper processing and textiles (Yang and Lee, 2005). Since it is applied predominantly in aqueous medium, it is released into the environment through wastewaters. EDTA is one of the organic pollutants found in highest proportions in surface waters in central Europe (Pietsch *et al.*, 1995*)*. The main application of EDTA is in cleaning products and detergents based on perborates as stabilizers and, in some countries, as an alternative to phosphates in detergent formulation.

EDTA has emerged as a persistent organic pollutant (Yuan and VanBriesen, 2006). It degrades to ethylenediaminetriacetic acid, which then cyclizes to the diketopiperizide, a cumulative, persistent organic environmental pollutant. EDTA exhibits low acute toxicity with LD_{50} (rat) of 2.0 - 2.2 g/kg (Hart, 2005). It was found to be both cytotoxic and weakly genotoxic in laboratory animals.

There is increasing concern about the direct or indirect potential effects of the presence of EDTA in the environment. Numerous field studies have shown that complexation with EDTA may mobilize contaminant metal ions. Attention has also been paid to the fact that EDTA can solubilize radioactive metals and increase their environmental mobility (Means and Crerar, 1978; Palumbo *et al.*,1994; Hakem *et al.*,2001). Another aspect to be considered is the possible contribution of EDTA in eutrophication water processes. Sillanpää (1997) warns that this phenomenon is relevant, since the molecule contains approximately 10% of nitrogen that could eventually be available to the aquatic microbiota. Although the isolated molecule is not present at risk of bioaccumulation, the ligand-metal complexes may significantly increase the bioavailability of extremely dangerous heavy metals. Vassil *et al.* (1998) studied the role of EDTA in the consumption of lead in a variety of mustard plants; discovered a concentrating effect of 75 times, which is highly significant if account is taken that it is a potentially dangerous phenomenon in terms of metal biomagnification processes. Dufková (1984) studied the interaction of EDTA with photosynthetic organisms and found that EDTA is toxic, since it inhibits cellular division, chlorophyll synthesis and algal biomass production. Free EDTA has shown to produce adverse reproductive and developmental effects in mammals. However, it is considered as a safe substance if used externally; which is relevant considering that EDTA is a common ingredient in cosmetic formulation (Lanigan and Yamarik, 2002). It has also been proved that heavy metals complexed with EDTA (and also with humic acids) are biologically available and toxic. This is demonstrated in the study of Tubbing *et al.*(1994) with river microalgae in which photosynthesis is inhibited at low concentrations of EDTA chelated with copper(II) (5-10 M) and unchelated EDTA. Guilhermino *et al.* (1997) found that Cd(II)-EDTA and Cu(II)-EDTA complexes were more toxic than their respective free metals in acute toxicity test in *Daphnia magna*. EDTA resistance to bacterial biodegradation is widely documented elsewhere (Allard *et al.*, 1996; Bolton *et al.*, 1993; Hinck *et al.*, 1996; Madsen and Alexander,1985). The compound is harmful to gram negative bacteria, causing the destruction of their outer membrane (Hancock, 1984; Tubbing *et al.* 1994). Most of the reports indicate that biological treatments are not efficient in the degradation of the chelate. Hinck *et al.* (1996) evaluated EDTA biodegradation in a complete study using four types of different sludge and found a total absence of EDTA degradation. The chelate passes unmodified through wastewater treatment plants because of its resistance to biodegradation and scarce adsorption onto the commonly employed adsorbents. Thus, in Swiss sewage treatment plants equipped with both chemical and biological treatment systems, it is found that no significant EDTA elimination is achieved (Kari and Giger, 1996; Nirel*et al.*,1998). Nirel *et al.*(1998) found that 10 of 12 domestic sewage treatment plants possessed significant of EDTA in their effluents. In industrial wastewater treatment plants, the chelate generally shows poor biological degradability (Hinck *et al.*, 1996; Witschel *et al.*, 1999) and presents two additional problems; it affects their efficiency to remove heavy metals and increases the charge of dissolved nitrogen in effluents. EDTA is undesirable in biological treatment systems specially of those used to achieve metal removal, because the ligand prevents bacterial metal adsorption phenomenon (Hafez *et al.*, 2002).

The EDTA complexed metallic species are found to be soluble over the entire pH region and showed enhanced mobility of these metallic species in solution, hence, the treatment of such metal-EDTA containing wastes is one of the important research endeavors (Nowack *et al.*, 1997).

1.2.2. Nitrilotriacetic acid(NTA)

Nitrilotriacetic acid (NTA) is a tertiary amino-polycarboxylic acid chelating agent that exists as a white crystalline powder at room temperature (HSDB, 2009), as described by Heintz (1862). It forms water-soluble complexes with many metals and reacts with strong oxidizing compounds(IARC,1990). Since 1960s, NTA generally replaced the phosphates in commercial detergents due to the increasing surface water eutrophication and its disastrous effect on natural aquatic environment (NCI, 1977).

The compound sequesters Mg and Ca ions present in hard water, thereby reducing buildup and scaling caused by salts of these ions (IARC, 1990). Although its use in detergents was suspended in the USA in 1971, this use was again resumed in the 1980s after phosphorous were banned from detergents. It is used as an eluting agent in purification of rare-earth elements, as a boiler feed water additives, in water and textile treatment, in metal plating and cleaning, and in pulp and paper processing (IARC, 1990; Vohra and Davis, 1997). To a lesser extent, the compound is used in leather tanning, photographic development, synthetic rubber production, the manufacture of pharmaceuticals, and in herbicides formulations and micronutrient solutions in agriculture (NCI, 1977; Sax and Lewis,1987)

The routes of potential human exposure to nitrilotriacetic acid are inhalation, ingestion, and dermal contact (HSDB, 2009). The population may be exposed through ingestion of drinking water or dermal contact with products containing nitrilotriacetic acid or its salts. In 1988, EPA's Toxics Release Inventory reported environmental releases of 13,000 lb of nitrilotriacetic acid, of which 20% was released to air, 40% to surface water, and 40% to on-site landfills (TRI, 2009).

NTA is present in drinking water primarily in the form of metal complexes, rather than as the free acid. The amount of NTA complexed with metal ions is dependent on the concentrations of the metal ion, $NTA^{3-}$and H^+, as well as the formation constants of the various complexes (Anderson *et al.*, 1985). Based on one model of NTA metal ion speciation, it is predicted that at a concentration of 25 ppb in river water, 50% of the NTA is complexed with Cu^{2+} ions, 34% with Ni^{2+}, 9% with Ca^{2+} and 5% with Zn^{2+}(McFuff and Mord, 1973) . Nitrilotriacetic acid itself is reasonably anticipated to be a human carcinogen on sufficient evidence of carcinogenicity in experimental animals (NCI, 1977; Goyer *et al.*, 1981; IARC, 1990&1999). Oral exposure of nitrilotriacetic acid caused urinary-tract tumors in mice and rats. Exposure to the free acid caused benign and/or malignant kidney tumors in mice of both sexes and in male rats, cancer of the ureter in male rats, and cancer of the urinary-bladder in female rats.

Exposure to the trisodium salt had the same effects in rats and also caused kidney tumors and cancer of the ureter in female rats (NCI, 1977; Goyer *et al.* ,1981). When administered in the diet, nitrilotriacetic acid induced kidney tubular cell adenocarcinomas in mice of both sex, kidney tubular cell adenocarcinomas or adenomas in male rats, papillomas or adenomas of the ureter in male rats, and transitional cell carcinomas of the urinary bladder in female rats. Increased incidences of pheochromocytomas of the adrenal gland and heptocellular adenomas were also reported for female rats.

1.2.3. Iminodiacetic acid (IDA)

Another common organic ligands found in industrial wastes is iminodiacetic acid (IDA) having chemical formula, $HN(CH_2CO_2H)_2$. IDA is a dicarboxylicamine. The iminodiacetate anion can act as a tridentate ligand to form a metal complex with two, fused, five membered chelate rings. The proton on the nitrogen atom can be replaced by a carbon atom of a polymer to create an ion-exchange resin such as chelex 100. IDA forms stronger complexes than the bidentate ligand glycine and weaker complexes than the tetradentate ligand nitrilotriacetic acid**.**

IDA is widely used as potential sequestering agent to control the metal mobility in the aquatic environment (Lee *et at.*, 2009a; US Patent, 1979). Because of high complexing capability, the polycarboxylic acids are much employed in the detergent industry as substitutes of phosphates (Nuttall and Stalker, 1977; Mailhot *et at.*, 1995). It was well augmented that the chelating resins comprising with variety of ligands forming selective and suitable bonds with several heavy metal toxic ions and making a suitable option for the attenuation of these metal ions from aqueous solutions [Ling *et at.*,2010; Shaw *et al.*, 2003; Stair and Holcombe, 2007). Further, because of available electron pairs and the tendency of forming stable covalent complexes with bivalent metals, chelating resins contained with iminodiacetic acid (IDA), for instance the commercial products, *viz*., Rohm & Haas (Amberlite IRC 748), Purolite (S930), Bayer (Lewatit TP 207) or tentatively synthesized by researchers Chelex-100 in Bio-Rad Laboratories, Richmond, were widely employed in the speciation or trapping of several heavy metal ions. The study was extensively studied for the various parametric factors including the effect of pH, time, ionic-strength, temperature, adsorption equilibrium, thermodynamics, kinetics, dynamics, competitive selectivity and regeneration etc. (Mumford *et al*., 2007; Yuchi *et al.*, 1997; Atzei *et al.*, 2001). The tap water was treated with the IDA impregnated cation exchange resins (Korngold *et al*.,1996); nickel loading and its selective attenuation was carried out using the iminodiacetic acid chelating resins (McKevitt and Dreisinger, 2012a & 2012b). Recent studies indicated that IDA is more useful in making the functionalized carbon nanotubes which were showed enhanced applicability in the sorption, pre-concentration of several heavy metal cations in a heterogeneous separation process (Wang *et al.,* 2011). Moreover, the silica capillaries were functionalized with the IDA and Cu(II) was immobilized in the selective proteins or peptide determination and separation. This was studied in an extension of the immobilized metal ion affinity chromatography as to make the miniaturization of the devices in the chromatographic column separation (Mehyou *et al.*, 2011; Gaberc-Porekar and Menart, 2001; Arevalo*et al.*, 2000). Additionally, the IDA was found to be enhanced applications as a chemical intermediates for the production of glycophosphate herbicides, electroplating solutions, chelating resin, surfactants, anticancer drugs etc. (Luo et al., 2009; Parker, 2003; Maurizia, 2006; Wasim and Brett, 2001; Juang and Wang, 2003). These diverse studies enabled the wide applications of IDA for the various detection/attenuation/separation purposes of many heavy metal toxic ions. Therefore, the presence of heavy metal complexed compounds are seemingly toxic in the water or soils and posing a serious threat towards the human being or plants. Moreover, the heavy metal-IDA complexed species showed high solubility and mobility in the aqueous solutions hence restricted its separation from the aqueous phase.

1.3. HEAVY METAL COMPLEXED SPECIES AS WATER POLLUTANTS

In marine and aquatic chemistry, metals are not entirely free and may occur as a range of complexes (Filella *et al.*, 1995; Turner, 2001). Synthetic organic ligands such as APCAs containing carboxylic groups connected to one or a few atoms of nitrogen are able to complex metal ions by formation around them one or a few stable heteroatom rings through the phenomenon known as *chelating*. The data available regarding concentrations of synthetic complexing agents in the aquatic environment has until now almost exclusively focused on the aminocarboxylates. The main examples are EDTA and NTA. EDTA includes six donor atoms and acts as a hexadentate ligand whereas NTA includes four donor atoms so it is a tetradentate ligand. EDTA and NTA form the complexes with metal ions of the molar ratio M(II):L=1:1. The complexes possess the octahedral structure. Formation of stable complexes with metal ions is the base of their application for analytical and industrial purposes. The complexes formed due to chelation are dissolved in water and metal ions found in them do not exhibit such chemical activity as uncomplexed ions. The stability of the complex formed depends mainly on the nature of the metal ion, the complexing agent, the pH value and the temperature.

Existence of such complexes in water bodies causes 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 as well as radionuclides from radioactive waste into the aquatic environment (Reinecke*et al.*, 2000).

It was stressed that most of the APCAs (such as EDTA-ethylene diaminetetraacetic acid, NTA-nitrilotriacetic acid, IDA-iminodiacetic acid, DTPA-diethylenetriamine pentaacetic acid) are resistant to conventional biological and physicochemical methods of waste water treatment and purification of drinking water. Degradation of EDTA and NTA in natural conditions proceeds due to growth of specific bacteria from the subclass of *Procteobacteria*. It was found that M(II)-EDTA complexes with the stability constants below 10^{12} such as Ba(II), Mg(II), Ca(II) and Mn(II) were degraded whereas chelates with higher stability constants such as Fe(III),Co(II), Cd(II), Pb(II), Ni(II) or Cu(II) were not metabolized (Nörtemann, 2005).

In spite of being cost-effective and efficient for treatment of metal-bearing effluents, chemical precipitation is ineffective for removing EDTA and DTPA due to the stability and solubility of their metal complexes (Vohra and Davis, 2000). When it is present in the form of metallic complex, EDTA renders heavy metal removal by precipitation more difficult due to an increasing solubility of its metal cations (Kelly and Sutton, 1966). Due to its recalcitrance, the toxicity of the metal complex prevents COD removal using biological processes, leading to a slow degradation of the target pollutant by microbes (Sillanpää and Sihvonen, 1997).

Treatment of wastewaters containing metal complexes, such as metal-EDTA is one of the research endeavors. Such complexed metallic species are found to be soluble over the entire pH region and showed enhanced mobility of these metallic species in solution (Nowack *et al.*, 1997). Decomplexation of metal-EDTA being the prerequisite in the treatment of metal-EDTA containing wastes as well as control of heavy metals, several techniques were demonstrated in the treatment of such wastes (Vanbriesen and Rittmann, 1999; Ridge and Sedlak, 2004; Lin and Juang, 2002; Prairie *et al.*, 1993; Davis and Green, 1999; Yang and

Davis, 2000a & 2000b). Literature survey reveals that the biodegradation of EDTA was carried out and the liberation of free metal ions showed lower mobility under neutral conditions (Vanbriesen and Rittmann, 1999). Ferric chloride was used to remove the copper and zinc in the municipal waste water in which these metal ions are complexed with EDTA (Ridge and Sedlak, 2004). The process was demonstrated that copper and zinc were adsorbed on ferric hydroxide; however, the waste was contained with soluble Fe-EDTA- species. TiO_2-mediated photocatalytic treatment was reported to deal with wastes containing EDTA-complexed metal ions (Prairie *et al.*, 1993; Davis and Green, 1999; Yang and Davis, 2000a & 2000b). Similarly, few reports dealt with the adsorption of metal-EDTA species onto the surface of TiO_2 solid (Yang and Lee, 2005). Non-dispersive solvent extraction process was also reported for the removal of EDTA complexed copper from aqueous solutions (Lin and Juang, 2002). These reported methods seem either expensive or inadequate for the complete treatment of wastes contaminated with metal complexed EDTA. Similarly, it was found that certain NTA complexes (Cu, Ni, Cd, Hg) are very resistant to bio-degradation (Chau and Shiomi, 1972). Therefore, because of the enhanced toxicity, mobility of metal ions and increased stability and resistance to degradation, these metal complexed organic species containing wastewaters need to be adequately treated prior to its discharge into the environment.

1.4. OVERVIEW OF CONVENTIONAL WASTEWATER TREATMENT

Although the collection of storm water and drainage dates from ancient times, the collection of wastewater can be traced only to the early 1800s and the development of the germ theory in the latter half of the nineteenth century by Koch and Pasteur marked the beginning of new era in sanitation. Today, a typical wastewater treatment system comprises of unit operations or physical treatment and unit processes referring to chemical treatments or biological treatments. The unit operations and processes 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 settle able 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 process, 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 have been long established in removing many chemical and microbial contaminants of concern to public health and the environment, the effectiveness of these processes has 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 have 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 been proven to successfully remove a wide range of potential water contaminants and hold great promise in water and wastewater treatment technologies.

1.5. OXIDATION PROCESSES IN WASTEWATER TREATMENT

1.5.1. 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-}.These oxidations are simple and the mechanisms only require contact of ozone with the ion. 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 have been classified as potentially carcinogenic 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 at 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.

Use of hydrogen peroxide

Hydrogen peroxide is another strong oxidant readily applied to wastewater treatment in the past. For wastewater applications 50% hydrogen peroxide solution is normally recommended while 35% solution gives lower rates though higher safety and 70% may produce detonable mixtures with many of the organic compounds. Hydrogen peroxide has been found to be effective in degradation of compounds or treatment of real wastewaters requiring less stringent oxidation conditions (Ayling and Castrantas, 1981) but applications to complex mixture of effluents like dyes, textile industry effluent, heteroaromatics etc. need to be explored.

A major problem encountered with the application of hydrogen peroxide alone for wastewater treatment applications are very low rates for applications involving complex materials, e.g., Fung *et al.*(2000) have shown that the degradation of CI reactive red 120 dye was marginal for treatment with hydrogen peroxide alone whereas Arslan and Balcioglu (2001) have shown that absolutely no degradation was observed for the addition of hydrogen peroxide alone for the dyehouse effluents. Also, there are no reports where hydrogen peroxide has been used for the treatment of mixture of compounds. Moreover, stability of

H_2O_2 remains a question, as the catalytic decomposition agents present in effluents compete with the pollutants and hence proper injection methods achieving rapid dispersal of hydrogen peroxide, needs to be devised (Ayling and Castrantas, 1981). Also, if free radicals are formed and taking part in the reaction, additional hydrogen peroxide usually recombines with the dissociated hydroxyl radicals, decreasing the overall rates of degradation.

1.5.2. 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 ($\cdot OH$), as the primary oxidant (Glaze, 1987). The $\cdot OH$ radical is among the strongest oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rates of contaminant oxidation. The generation of $\cdot OH$ radicals is commonly accelerated by combining ozone (O_3), hydrogen peroxide (H_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 the early 1980s. However, the O_3–UV process is now considered less economical compared with 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. By varying test water quality, it was also confirmed that carbonate–bicarbonate ions and humic substances influenced significantly the oxidation rate.

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 the 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.), one of them will predominate. 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).

1.6. FERRATE(VI)

Iron commonly exists as metallic iron (Fe), ferrous (Fe^{2+}), and ferric (Fe^{3+}) forms in the natural environment. However, the presence of higher oxidation states of iron, i.e., +4, +5, +6 and +8 has been 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. Fe(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 Fe(VI) by Schreyer and coworkers (Thompson *et al.*,1951; Okerman and Schreyer, 1951). In the late 1950s, the chemistry of Fe(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 Fe(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, Fe(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, Fe(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 Fe(VI) was also confirmed in an aqueous solution by isotopic oxygen exchange study which showed that four oxygen atoms of Fe(VI) were kinetically equivalent (Goff *et al.,* 1971). Fe(VI) ions could possess three resonance hybrid structures in aqueous solution as shown in the following figure 1.1 (Norcross *et al.,* 1997). Of the three resonance structures, the structures '1' and '2' were suggested as main contributors of Fe(VI) based on theoretical studies of metal oxide structures.

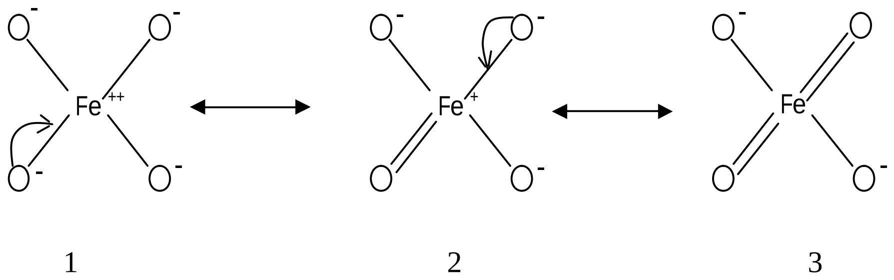


Figure 1.1. *Three resonance hybrid structures of Fe(VI) ion in an aqueous solution (Norcross et al., 1997)*

ii. Species in Aqueous Solution

Spectroscopic and kinetic studies have suggested that there exist four Fe(VI) species in aqueous solution via their acid-base equilibrium (Rush *et al.,*1996). The species distribution of Fe(VI) as a function of pH is indicated in the following figure 1.2 which indicates that $HFeO_4^-$ and FeO_4^{2-} are predominant species in neutral and alkaline pH solution in which Fe(VI) is known to be relatively stable towards its spontaneous decomposition to ferric ion (Fe(III)) (Lee and Gai, 1993).

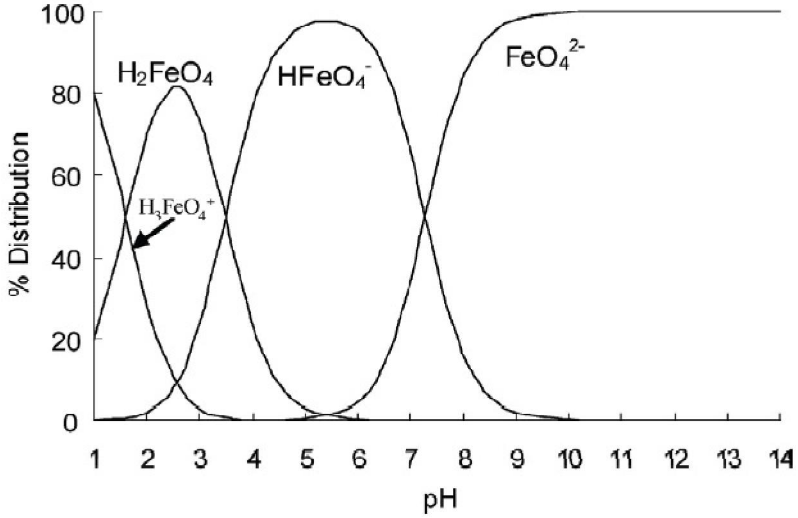


Figure 1.2. *Species distribution of Fe(VI) in aqueous solution (Tiwari et al., 2007)*

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 1.3 shows the UV-Vis absorbance spectrum in phosphatebuffer solution (pH 9.2) as a function of Fe(VI) concentration. 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 Fe(VI) at the wavelength of 510nm was conveniently used to measure the concentration of Fe(VI) in aqueous solutions (Sharma, 2002)

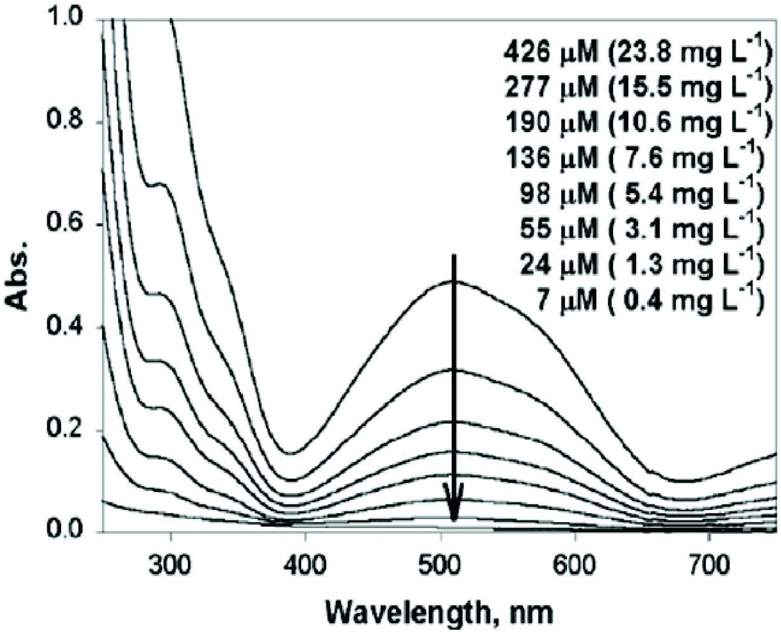


Figure 1.3. *UV-Vis absorption spectrum of Fe(VI) in aqueous solution as a function of its concentration, pH = 9.2, 25 mM phosphate buffer (Lee et al., 2004)*

iv. Stability and decomposition of Ferrate(VI)

The stability of ferrate(VI) of its 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 Fe(VI) seems to be more stable than concentrated (Schreyer and Okerman, 1951). The solution of 0.025M Fe(VI) will remain 89% even after the 60 min but if the initial concentration of Fe(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 0.01M potassium ferrate solution decomposed to 79.5% over a period of 2.5 h, while a 0.0019M 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 10M 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 1.4 obtained with using the 1mM solution of K_2FeO_4 in aqueous solution showed that at pH ~5, just after 7 min, the Fe(VI) was decomposed completely, however, at pH ~9 and ~10, 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 6M KOH, but decreased rapidly when it was in 3M KOH. The ferrate solution prepared with buffer solution at pH 8 was more stable than that prepared at pH 7 (Schreyer and Okerman, 1951); 49% of the original potassium ferrate remained after 8 h when the pH was 7, and 71.4% of that remained after 10 h when the pH was 8.

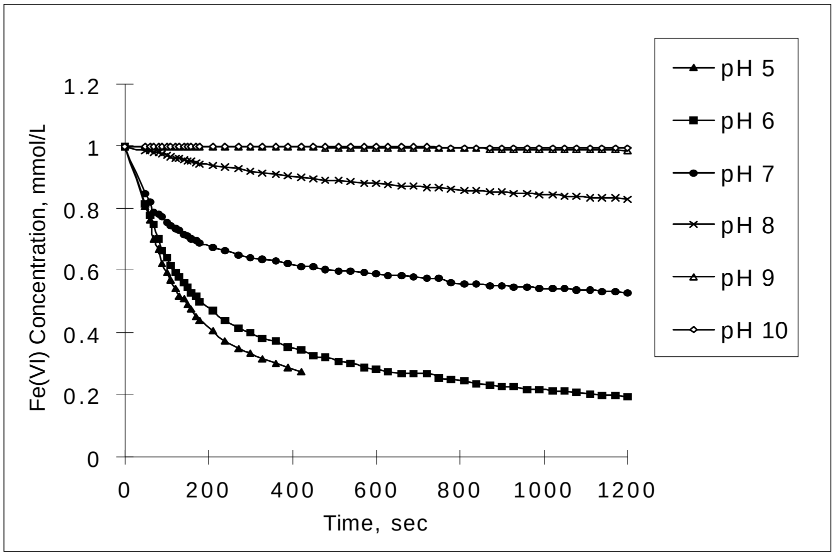


Figure 1.4. *The change of the Fe(VI) concentration as a function of time at various pH values[Initial concentration of Fe(VI): 1 mM] [Tiwari et al,. 2007]*

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) has already seen that it is strongly pH dependent. The lowest rate of decomposition occurred at pH higher than ~9-10, 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).*

$$2H_3FeO_4^{+} \leftrightarrow [H_4Fe_2O_7]^{2+} + H_2O \qquad k_2 = 3.5\text{x}10^5\ M^{-1}\ s^{-1} \qquad \ldots (1.2)$$

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

$$H_3FeO^{4+} + H_2FeO_4 \leftrightarrow [\text{diferrate}] \qquad k_4 \approx 3.5\text{x}105\ M^{-1}\ s^{-1} \qquad \ldots (1.4)$$

$$2H_2FeO_4 \leftrightarrow [\text{diferrate}] \qquad k_5 = 1.5\text{x}104\ M^{-1}\ s^{-1} \qquad \ldots (1.5)$$

$$H_2FeO_4 + HFeO^{4-} \leftrightarrow [\text{diferrate}] \qquad k_6 \approx 1.5\text{x}104\ M^{-1}\ s^{-1} \qquad \ldots (1.6)$$

$$2HFeO^{4-} \leftrightarrow [Fe_2O_7]^{2-} + H_2O \qquad k_7 = 2.5\text{x}102\ M^{-1}\ s^{-1} \qquad \ldots (1.7)$$

Reactions clearly showed that the forward reactions (1.2) to (1.7) except reaction (1.3) are relatively slow steps hence, could be the rate determining steps. The rate constants were then calculated for the self decomposition of Fe(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 1.5 (Rush *et al., 1996).*

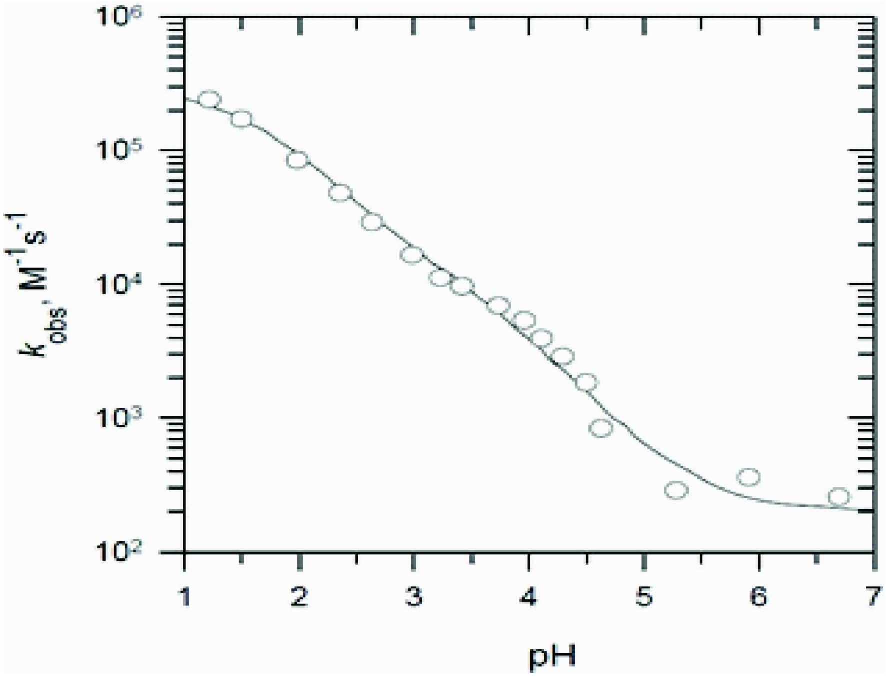


Figure 1.5. *The second-order rate constants for the decay of ferrate(VI) to iron(III) in 5 mM (phosphate/acetate) buffers (Rush et al.,1996)*

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

Ferrate(VI) is an emerging multi-purpose wastewater treatment chemical owing to its multifunctional properties, *viz.*, oxidation, disinfection, coagulation and generation of environmentally safe by-products. This unique property of Fe(VI) was first proposed by Murmann and Robinson (1974). The oxidative properties of Fe(VI) forms the basis for its potential applications, in particular to the environmental remediation. Fe(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 and 14, respectively. Under the acidic conditions, the redox potential of Fe(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 Fe(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 oxidation with Fe(VI) demonstrated that Fe(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 (Sharma *et al.*,1992; 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, Fe(VI) also effective in the degradation/removal of several inorganic contaminants, *viz.*, cyanide, ammonia, hydrogen sulphide etc. (Sharma *et al.*,1998a &1998b). Fe(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) has inactivated 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 Fe^{VI} reduction). Treatment of water by Fe(VI) could efficiently reduce 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, Fe(VI) further replaces several chemicals utilized for odor control of sludge, mainly aggressive odors caused by ammonia and sulphides (De Luca *et al.,* 1996). Fe(VI) being environmentally safe, showed effectiveness in controlling bio-film growth in condenser systems (Fagan and Waite, 1983) suggesting the usefulness of Fe(VI) as a biocide in controlling biofouling.

As such, Fe(VI) was proved to possess multifunctional properties in the wastewater treatment. Besides being strong oxidant, effective disinfectant, coagulant and antifouling agent, Fe(VI) is further termed as a ‘Green Chemical’ as the end product of Fe(VI) treatment is non-toxic, environmentally benign species, i.e., Fe(III) as seen in equation 1.1. This green nature of Fe(VI) is particularly interesting in environmental remediation making it a highly promising alternative candidate for replacing environmentally hazardous chemicals/oxidants often to use 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 Fe(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, Fe(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 Fe(VI), therefore, demonstrated Fe(VI) as a promising tool for an enhanced wastewater treatment to eliminate various organic or even inorganic impurities by Fe(VI)-oxidation as well as to remove non-degradable impurities by Fe(III) precipitation in a single treatment step. The use of Fe(VI) may, therefore, provide a safe, convenient, versatile and cost effective alternative to current approaches for water, wastewater, and sludge treatment. Fe(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

1.7. SCOPE OF THE PRESENT INVESTIGATION

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 can 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 extensively used, these chemicals have limitations and their use showed additional environmental concern due to the formation of toxic disinfection byproducts, excessive sludge and onsite odour etc. These limitations combined with the increasing levels of water pollution, clean/fresh water shortages and more stringent regulatory standards of drinking water and wastewater led to the search for a more effective, viable and environmentally benign oxidant and coagulant.

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, Fe(VI) was repeatedly demonstrated to be very effective treatment chemical in all sorts of water and wastewater systems. However, although, Fe(VI) showed effective and efficient for the removal of various species of organic pollutants and free metal species, only limited studies were conducted on the on the treatment of metal complexed species present in the aquatic environment.

The heavy metal toxic ions are reported to be in the complexed form with several complexing agents, *viz*., EDTA (Ethylenediaminetetraacetic acid), IDA (Iminodiacetic acid), NTA (nitrilotriacetic acid etc.), enhances the mobility of these contaminants in the water bodies. Moreover, due to higher stability over wide pH range poses serious problem for treatment processes. In view, the treatment of such wastes received a greater attention during recent past. Earlier, application of Fe(VI) in the treatment of waste containing cyanide complexed with copper and nickel was studied and was showed that Fe(VI) could substantially decrease the concentrations of cyanide and copper whereas the nickel concentration was decreased partly in the treated waste samples (Tiwari *et al.*, 2006). Recently, a research was carried out on Cu(II)-EDTA system, and it was found that Fe(VI) degraded the EDTA in the acid catalyzed degradation process and at the same time by flocculation/adsorption, Cu(II) was also removed effectively (Yang *et al.*, 2007). Our recent studies showed that the Fe(VI) could degrade heavy metals complexed systems, such as Cu(II)-EDTA, Zn(II)-NTA and simultaneously remove free metal ions through co-precipitation/coagulation effectively (Tiwari *et al.*, 2008, Yang *et al.*,2010).

Hence, keeping in view of the need to extend studies and to explore the applicability of Fe(VI) in the treatment of wastewater contaminated with organo metallic complexes, the present investigation deals with a systemic study of the Fe(VI) treatment for the degradation of organic complexing agents such as EDTA, NTA and IDA in single systems and as in complexed systems with heavy metal ions, such as Cu(II), Cd(II), Zn(II) and Ni(II).

CHAPTER 2

Review of Literature

2. REVIEW OF LITERATURE

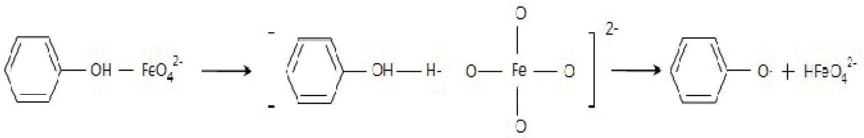
Research studies have demonstrated that Ferrate(VI) is quite effective in the removal of various types of impurities in municipal/industrial wastewaters (Tiwari*et al.,* 2005). The applicability of ferrate (VI) as disinfectant in wastewater treatment was investigated much earlier in 1974 (Murmann and Robinson, 1974) and also used by others as well (Gilbert, 1975; Schink and Waite, 1980; Waite, 1979; Jiang, 2007). Selective oxidations by ferrate(VI) was utilized in synthesizing organic compounds without producing toxic by-products (Southwell, 2003). Ferrate(VI) can complete the oxidation reactions in shorter time intervals than the oxidations carried out by permanganate and chromate (Delaude and Laszlo, 1996; Khalilzadeh*et al.,* 2007). Iron, unlike chromium and manganese, is considered non-toxic; therefore, ferrate(VI) can make industrial processes more environmentally benign by achieving cleaner technologies for organic syntheses as well. Ferrate(VI) 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 (Krasner *et al.,* 1989; Miao and Tao, 2008; Sharma, 2004 & 2010a; Zhou *et al.,* 2009). Like ozone, Fe(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). Ferrate(VI) also acts as a strong oxidant to degrade a wide range of compounds present in wastewater and industrial effluents (Carr *et al.,* 1985; DeLuca *et al.,* 1983; Li *et al.,* 2009; Yngard *et al.,* 2007).

Literature survey reveals that Fe(VI) oxidizesvarious synthetic organic compounds, *viz.,* benzene, chlorobenzene, allylbenzene and phenol, etc. (Bielski*et al.,* 1994; Gilbert, 1975; Waite, 1978). Fearrate(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 Fe(VI) was reported to be relatively fast and the increase of Fe(VI) dose favored the decomposition of these compounds. The reaction mechanism proposed with Fe(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 Fe(VI) to Fe(V) by its reaction with hydrated electron (e_{aq}-), (reaction (3.1)). Further, studies showed that Fe(VI) could be reduced to Fe(V) through one electron transfer by its reaction to organic radical compounds, which was well-known one-electron reductants (reaction (3.2)) and reaffirmed with their pulse radiolysis and fast spectroscopic results (Bielski, 1991 & 1992; Rush and Bielski, 1986).

$$FeO_4^{2-} + e_{aq}^{-} \rightarrow FeO_4^{3-} \quad \ldots (3.1)$$

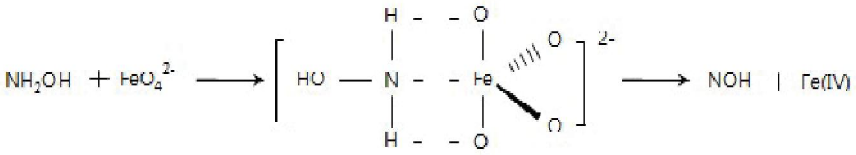
$$FeO_4^{2-} + R\dot{C}OH \rightarrow HFeO_4^{2-} + RCO \quad \ldots (3.2)$$

Similarly, the reaction of phenol with Fe(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 tha tthe oxidation of phenol by Fe(VI) proceeded through an intermediate radical species which was presumed as phenoxy radical (reaction (3.3)) (Huang *et al.*, 2001).



… (3.3)

Further, the two-electron transfer mechanism of Fe(VI) was proposed for the degradation ofseveral 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 (3.4)). 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).



… (3.4)

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 Fe(VI) was known to be stable. Moreover, the dominant species of the Fe(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 Fe(VI) and rate law for each reactant was found to be pseudo-first-order studied with an excess dose of Fe(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 Fe(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) werestudied 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).

Fe(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 process. 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 Fe(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 (3.5):

$$-d[Fe(VI)]/dt = k_P[Fe(VI)][P] \qquad \ldots (3.5)$$

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 (3.6 and 3.7) (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 (3.6)). This was different from the second-order rate law observed for the reaction of Fe(VI) with other cyanides (CN^-, SCN^-, $Cu(CN)_4^{3-}$ and $Ni(CN)_3^-$) (Sharma *et al.*, 1998b; 2002 & 2005a; Yngard *et al.*, 2007).

$$-d[Fe(VI)]/dt = k_P[Fe(VI)][M(CN)_4^{2-}]^{0.5} \text{where M= Cd(II), Zn(II)} \qquad \ldots (3.6)$$

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).

$$-d[Fe(VI)]/dt = k_P[Fe(VI)][SeO_3^{2-}] + k_2 [Fe(VI)][SeO_3^{2-}]^2 \quad \ldots (3.7)$$

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 wa sproposed that thiourea and thioacetamide were converted into sulphate at pH 9.0 using ferrate(VI). The stoichiometric ratios of Fe(VI) and thiourea and thioacetamide was found to be 1:0.38±0.02. Moreover, the proposed reaction was suggested as equations (3.8) and (3.9).

$$8HFeO_4^- + 3NH_2CSNH_2 + 9H_2O \rightarrow 8Fe(OH)_3 + 3NH_2CONH_2 + 3SO_4^{2-} + 2OH^- \ldots (3.8)$$

$$8HFeO_4^- + 3CH_3CSNH_2 + 9H_2O \rightarrow 8Fe(OH)_3 + 3CH_3CONH_2 + 3SO_4^{2-} + 2OH^- \ldots (3.9)$$

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). Ata dose of 0-50 ppm as FeO_4^{2-}, the bacteria were removed completely. The oxidation of *E. Coli* DNA *polymerase-I* by Fe(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 Fe(VI) cuased DNA chain cleavage through a mechanism in which base loss was followed by β-elimination at the abasic 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 kill of *E. coli* (Gilbert*at 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 /100mL) were used to assess the Fe(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 Fe(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 thatferrate(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 pH6.9 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 Fe(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 Fe(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) oxidizes 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 Fe(VI) required to oxidize three moles of As(III) (reaction 4**.**0). The oxidation of As(III) followed second order rate law at pH 8.4 to 9.0. It was noted that the complete oxidation took place within a second.

$$2\text{Fe(VI)} + 3\text{As(III)} \rightarrow 2\text{Fe(III)} + 3\text{As(V)} \qquad \ldots (4.0)$$

Further, it was demonstrated that with even smaller dose of Fe(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 Fe(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 contain 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 Fe(VI) and showed that Fe(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 Fe(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 pre oxidation step of the treatment (Ma and Liu, 2002a & 2002b; Ma *et al.,* 2008a & 2008b). In the pre oxidation 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 Fe(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 Fe(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).

Reports indicated that Fe(VI)can, perhaps, replace several chemicals utilized for odor control of sludges, mainly aggressive odors caused by ammonia and sulphides; through the formation of precipitates with iron compounds. Ferrate (VI) applied to sludge treatment as well and showed a double effects such as transforming the ammonia and sulphur containing compounds into nitrates and sulphates, respectively; acting as an electron acceptor therefore, preventing the development of further odors when biosolids were treated (De Luca *et al.*, 1996). Similarly, it was found that potassium ferrate(VI) is much effective over lime in oxidizing reduced sulphur and nitrogen compounds and also mitigating odors from conditioned sludge.

The addition of ferrate(VI) in the photocatalytic process, it appears to significantly enhance the photocatalytic degradation of microcystin-LR using TiO_2 (Yuan *et al.* 2002). Potassium ferrate(VI) also exhibits good potential to be an oxidant for the removal of sulfamethoxazole (SMX), a worldwide-applied antibacterial drug (Sharma *et al.*, 2005a).

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 complexed were carried out and showed that complete degradation of cyanide along with the complete removal of free copper and partial removal of nickel was achieved from the Fe(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 Fe(VI) for treating the mixed systems containing the organic ligand species with heavy metal toxic ions. Decomplexation of Cu(II)-EDTA system by Fe(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 Fe(VI), such as $HFeO_4^-$ and H_2FeO_4, which are relatively more reactive than the un-protonated 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 Fe(VI) concentration. Similarly, in the case of Zn(II)-NTA system, the decomplexation by Fe(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 suggests that Fe(VI) prefers 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 Fe(VI) was investigated with variation of solution pH from 8 to 12 (Yu *et al.*, 2012). At pH 8, a rapid Fe(VI) reduction was observed in initial reaction time but much reduced Fe(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 Fe(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 Fe(VI) occurred as within few minutes of contact time, maximum cadmium was removed.

CHAPTER 3

Methodology

METHODOLOGY

3.1. Materials

3.1.1. Chemicals and Apparatus

The chemicals used for the experiments were of AR/GR grade. Iminodiaecetic acid ($C_4H_7NO_4$), nitrilotriacetic acid ($C_6H_9NO_6$), iron(III) nitrate nanohydrate ($Fe(NO_3)_3.9H_20$), diethyl ether ($C_4H_{10}O$), hexane, (C_6H_{14}) were obtained from Sigma Aldrich. Co., USA. potassium hydroxide (KOH), nickel(II) sulphate heptahydrate ($NiSO_4.xH_2O$), zinc chloride ($ZnCl_2$), copper sulphate pentahydrate ($CuSO_4.5H_2O$), hydrochloric acid (HCl), sodium chloride (NaCl), sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$), sodium sulphite (Na_2SO_3), sodium sulphate (Na_2SO_4), sodium phosphate (Na_3PO_4), phosphoric acid (H_3PO_4) were obtained from Merck India Ltd., India. Disodium ethylenediamine tetraacetic acid ($C_{10}H_{14}N_2Na_2O_8.2H_2O$), cadmium nitrate ($Cd(NO_3)_2.4H_2O$) was procured from the Loba Chemie, India. Moreover, the disodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$), 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), obtained from Millipore Water Purification system (Model: Elix 3) was used for entire solution preparations and other analytical studies. Standard solutions of opper, zinc, cadmium and nickel (1000 ppm) were obtained from Merck. These solutions were diluted and used for calibration of AAS.

Glass Filtration System with fritted funnel (10-15µ) obtained from Merck, India Ltd. and Whatman Filter Paper (GF/C grade, 47mm) were used for filtration during Ferrate(VI) preparation. Syringe filter of 25 mm diameter in size and porosity of 0.47 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 (*EUTECH Instruments; Model: Cyberscan pH 310, pH/MV/°C/°F Data meter*) was used for entire pH measurements in aqueous solutions. Before using the pH meter, it was calibrated with the known buffer solutions.

3.1.2. Reagents

i. Sample Stock solutions: 0.01M solution of different metal complexes.
ii. Standard Buffers (pH 4.01, 7.00 & 12.45) for calibrating pH meter.
iii. HNO_3 and NaOH for adjusting pH of the sample solutions.

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

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

UV-Vis spectrometer was used to measure the absorption of light intensity at particular wavelength of incident light. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels. For visible and ultra violet spectrum, electronic excitation occurs in the range 200-800nm and involves the promotion of electrons to the higher energy molecular orbitals. UV-Vis spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert's law which states that '*the absorbance of the solution containing light absorbing species at a particular wavelength is directly proportional to the concentration of the solution into path length of the sample cell(cm)*'.

The principle of this technique lies to the fact that molecules containing 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.

The alternative title of this technique is Electronic Spectroscopy since it involves the promotion of electrons from the ground state to the higher energy states. The amount of light absorbed by the sample is as a function of the wavelength (nm unit) is called the absorption spectrum which generally consists of absorption bands. For visible and 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 rotatory motion of the molecules (Hollas, 2005). Since the energy levels of a molecule are quantized, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation.

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

3.1.4. Atomic Absorption Spectrophotometer (AAS)

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

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

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

3.1.5. Total Organic Carbon Analyser (TOCA)

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

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

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

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

Whether the analysis of TOC is by TC-IC or NPOC methods, it may be broken into three main stages, *viz.*, acidification, oxidation and Detection and quantification. The first stage, that is, addition of acid and inert-gas sparging allows all bicarbonate and carbonate ions to be converted in to carbon dioxide, and this IC product vented along with any POC that was present. The release of these gases to the detector for measurement or to the air is dependent upon which type of analysis is of interest, the former for TC-IC and the latter for TOC (NPOC). The second stage is the oxidation of the carbon in the remaining sample in the form of carbon dioxide (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-VCPH/CPN) employed for the present investigation is based on 680°C combustion catalytic oxidation/NDIR method, developed by Shimadzu and the model is highly sensitive, capable of measuring parameters such as TC, IC, TOC, NPOC with measuring range and detection limit as TC:0 to 25000 and IC:0 to 30000 and 4 µg/L, respectively. The 680°C combustion catalytic oxidation method achieves total combustion of samples by heating them at 680°C in an oxygen-rich environment and the TC combustion tube is filled with a platinum catalyst. Since this utilizes the simple principle of oxidation through heating and combustion, pretreatment and post-treatment using oxidizing agents are unnecessary, which enhances operability. The carbon dioxide generated by oxidation is detected using an infrared gas analyzer (NDIR). By adopting a newly-designed, high-sensitivity NDIR, the TOC-L series achieves high detection sensitivity, with detection limit of 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 TC (total carbon) in the sample is obtained through comparison with a calibration curve formula. Furthermore, by subjecting the oxidized sample to the sparging process, the IC (inorganic carbon) in the sample is converted to carbon dioxide, and the IC concentration is obtained by detecting this with the NDIR. The TOC concentration is then calculated by subtracting the IC concentration from the obtained TC concentration.

3.1.6. Ion Chromatograph

Ion chromatograph (*Metrohm, Modular IC System*) was employed for the study of the decomplexation of organometallic complexes.

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

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

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

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

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

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

3.1.7. Inductively Coupled Plasma

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

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

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

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

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

3.2. Analytical Methods

3.2.1. Preparation of Ferrate(VI)

Ferrate(VI) as Potassium ferrate (K_2FeO_4) was prepared by adopting wet chemical oxidation method, with some modifications as described elsewhere (Li *et al*., 2004; Tiwari *et al*., 2007). The Fe(III) was oxidized into Fe(VI) using the sodium hypochlorite (12-14%). The detailed preparation process is described as: 300 ml of chilled NaClO solution was taken in a beaker and 90 g of solid KOH was added slowly in this solution and the resulting suspension was again cooled. The precipitate formed was filtered with GF/C filter paper, to give a clear yellow and highly alkaline NaClO solution. The solution was chilled and filtered using a GF/C filter paper to remove any precipitates occurred from the solution. To this solution, 20g of pulverized ferric nitrate was added slowly within *Ca.* 2 hours, with constant and vigorous stirring under cold conditions (< 8° C). Further, after the complete addition of the ferric nitrate, the solution was stirred for another *Ca*. 30 minutes. It was noted that the cold and highly alkaline conditions favored the oxidation of Fe(III) to Fe(VI). Also the time allowed for stirring may result in enhanced yield. The color of the solution readily changed to purple showed the formation of Fe(VI). Further, *Ca.* 50 g of solid KOH was added slowly; with maintaining the solution temperature ≤ 15° C. The solution mixture was allowed to cool by standing in a refrigerator for *Ca.* 40 mins. The resulting dark purple slurry was filtered with a glass filter (medium porosity 10-15μm) and the filtrate was discarded. The precipitate was washed with cold 3M KOH solution (*Ca*. 100mL (20mL×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 Fe(VI). Finally, the solid was flushed with n-hexane (four times×10 mL) and diethyl ether (two times × 10 mL). The final product was collected carefully, it was almost black in color and stored in a vacuum desiccator (figure 2.1) along with NaOH pellets.

Figure 2.1. *Dark purple solid K_2FeO_4*

3.2.2. Determination of the purity of the prepared Fe(VI)

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

$$A = \varepsilon . b . c \qquad ...(2.1)$$

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

ε = molar extinction coefficient of Fe(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 Fe(VI) (mol/L)

$$, \quad \% \quad (\quad) = \frac{. \times 100\%}{. \quad (1 \times 10 \quad)}$$

The purity of Fe(VI) was found to be > 95 %. Actual amount of Fe(VI) was always taken, in each experiment, based on the purity percent obtained to compensate for the impurities present.

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

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

Batch experiments were first performed for the single systems. The degradation of organic species in single systems by Fe(VI) was studied as a function of molar concentrations of Fe(VI) and time at different but constant pH values. 2.0 x 10^{-4}mol/L of IDA solution was first prepared using phosphate buffer pH 10. In case any slight change in pH occurred, the solution pH was again adjusted by addition of drops of H_3PO_4/NaOH. A known amount of Fe(VI) was then added to this solution such that the resulting solution was having molar concentration of Fe(VI) as 0.5 x 10^{-4}mol/L. Then, absorbance of the sample solution was immediately recorded at 510 nm using UV-Vis spectrophotometer at regular interval of time for 30 minutes. Absorbance for the blank, i.e., Fe(VI) in buffer solution was also recorded for the same intervals of time and period as to observe the self-decomposition of Fe(VI) in the studied medium. Further, the absorbance of sample was corrected with the blank data. Again, the experiment was repeated increasing the concentration of Fe(VI) from 0.5 x 10^{-4}mol/L to 7.0 x 10^{-4} mol/L for the same concentration of IDA i.e., 2.0 x 10^{-4}mol/L. The recorded absorbance were related to the change in concentration of Fe(VI) and always necessary corrections were conducted using the blank data obtained at that concentration and medium as well. Similar experiments were performed for EDTA system taking molar ratios of EDTA and Fe(VI) as 2:0.5, 2:1, 2:2, 2:3, 2:5, 2:7 wherein the concentration of EDTA remains constant at 2.0 x 10^{-4} mol/L. Similarly, degradation of NTA in presence of Fe(VI) was studied in various concentrations of Fe(VI) as a function of time at different but constant pH values. Batch experiments were again performed as above by treating 1.0 x10^{-4} mol/L of NTA solution with varying doses of Fe(VI), from 0.5x10^{-4} mol/L to 15.0 x 10^{-4} mol/L.

In case of complex systems, the degradation of organic species/decomplexation of the metal complexes were investigated as a function of molar concentration of the metal complex species and different time intervals keeping constant but different solution pH. Batch experiments were first performed for Cu-IDA system. 0.01mol/L aqueous stock solution of Cu-IDA was prepared using $CuSO_4$ salt and IDA which was then diluted and the solution pH 8 was adjusted to 8.0 by the addition of concentrated NaOH (1 mol/L) solution. Further, a series of 100 mL (each) of Cu-IDA solutions having different Cu(II) to IDA molar ratios ranging from 0.5 to 15.0 mmol/L were obtained. The pH of these solutions was again checked and adjusted to pH 8 by drop wise addition of concentrated NaOH. Then, a known quantity of Fe(VI) was carefully weighed and introduced into these sample solutions (the weight of Fe(VI) was taken so as to obtain 1.0 mmol/L of Fe(VI) in the sample solution). The resulting solutions were quickly taken into the UV-Visible spectrophotometer and the absorbance reading at 510nm was recorded at the interval of 1 min for a period of 20 mins. Similar, observations were obtained for all the samples prepared previously. Absorbance of

Fe(VI) in blank buffer solution at pH 8 were also recorded for necessary absorbance correction to compensate for self-decomposition of Fe(VI). Before recording absorbance of the sample solution, the UV-Visible Spectrophotomer was always calibrated using the aqueous solution prepared at that pH. The similar experiments were repeated at different pH values, i.e., pH 9.0, 10.0, 11.0 12.0. Similarly, for other metal complex systems i.e., Cu(II)-NTA, Cu(II)-EDTA, Zn(II)-IDA, Zn(II)-NTA, Zn(II)-EDTA, Ni(II)-IDA, Ni(II)-NTA, Ni(II)-EDTA, Cd(II)-IDA, Cd(II)-NTA and Cd(II)-EDTA were studied for the decomplexation and degradation of organic impurities using a constant dose of Fe(VI). The UV-Vis data obtained for the degradation of Fe(VI) were then employed for the kinetic studies i.e., the time dependence data was simulated for the pseudo-first and pseudo-second order rate laws to its standard form.

The samples (single and complexed systems), once after obtaining the UV-Vis data, were further stirred for 2 hrs and then filtered using 0.45 μm syringe filter and subjected for other analysis viz., TOC and AAS. Always a blank sample was used for required comparison in analysis.

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

Complementary to the UV-Visible measurements, the study of the degradation level of organic species in the same systems under section 3.2.3 was extended in terms of TOC measurements by assessing the total organic carbon content of the sample solutions before and after treatment with Fe(VI) to correlate with the decomposition percent of the organic impurities. The TOC value for each of the above sample solutions with its corresponding blank solution i.e., in the absence of Fe (VI) was measured with the help of TOC analyzer (Shimadzu, TOC-VCPH/CPN). The decrease in TOC value indicates the extent of the decomposition of the organic species under study due to Fe(VI) treatment.

Similarly, the degradation of organics in the complexed systems was obtained using the TOC analysis. The blank solutions were also analyzed for TOC for necessary corrections. Hence, the corrected values inferred to the degradation of NTA in solution.

3.2.5. Removal of metals (AAS/ICP measurements)

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

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

$$\% \qquad = ((\qquad)/\quad) \times 100 \qquad \ldots (2.2)$$

where, : Initial metal concentration

: Metal concentration of treated sample

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

The study of the degradation of metal complexes due to Fe(VI) treatment is extended with direct measurement of the dissociated anions using ion chromatograph *(Metrohm Modular IC System).*

pH dependence of the decomplexation of Cu(II)-EDTA was also studied with the help of IC measurements. 0.10 mmol/L of Cu(II)-EDTA was treated with 2.4 mmol/L of Fe(VI) at different pH values, for 60 minutes of total reaction time. The ionic strength of the solution was maintained at 0.01 M with $NaNO_3$. The solution pH was maintained within ±0.1 of the desired value using the 0.01 M NaOH or 0.01 M HNO_3 during the reaction period. Aliquots of the solution were periodically removed from reactors and rapidly filtered through 0.45 μm membrane filters and the change in concentration of Cu(II)-EDTA was checked with the help of ion chromatograph (Metrohm Modular IC System) which was calibrated previously with the known concentrations of Cu(II)-EDTA at the same pH. The results were obtained as a function of time and at different pH values. The IC measurements for other samples were not continued because of the difficulty occurred as the column used to get choked in presence of small sized floc particles of Fe(III).

3.2.7. Effect of background electrolytes and ionic strength

The effect of background electrolytes on the reduction efficiency of Fe(VI) in presence of different metal complexes was investigated using seven different types of electrolytes, *viz.*, $NaNO_3$, $NaNO_2$,Na_2SO_3, Na_2SO_4, NaCl, $NaClO_4$ and Na_3PO_4. A sample solution of metal complex ($1x10^{-4}$ mol/L) was prepared using phosphate buffer and to it, a known amount of electrolyte was added such that the resulting solution contains molar ratios of metal complex to electrolyte as 1:1. Using drops of H_3PO_4/NaOH, the solution was adjusted to pH 10.0. Then, a known amount of Fe(VI) was added so as to achieve the concentration of Fe(VI) as $1.0x10^{-4}$ mol/L, *i.e.*, the stoichiometric ratios of 1:1:1 for metal complex, electrolyte and Fe(VI). The change in concentration of Fe(VI) in the solution was observed by recording the absorbance of the solution at the wavelength of 510 nm using UV-Visible spectrophotometer at regular time interval for a specified period. Similarly, absorbance of blank solution, i.e., in absence of metal complex and electrolyte was also recorded for comparison and necessary correction, if needed.

In order to further investigate the effect of ionic strength on the reduction efficiency of Fe(VI) as a function of time, Zn(II)-NTA system was also taken for this study. Zn(II)-NTA solution (1.0×10^{-4} mol/L) containing varying concentrations of $NaNO_3$ ranging from 1.0 mmol/L to 1.0 mol/L were taken in different beakers and the pH of each solution was adjusted to 9.2 by addition of drops of conc. HNO_3/NaOH solutions. Then a known amount of Fe(VI) for achieving ferrate dose of 1.0×10^{-4} mol/L was added to the solution. The change in concentration of Fe(VI) as a function of time was checked with the help of UV-Visible spectrophotometer (Thermo, UV1). The same experiment was repeated for remaining solutions containing different $NaNO_3$ concentration. The change in total zinc concentration was checked after filtration of Fe(VI) treated samples using 0.45 µm syringe filter and was analyzed by an inductively coupled plasma (Optima 2000 DV, Perkin-Elmer). The degradation of NTA was measured by TOC (total organic carbon) analyzer.

CHAPTER 4

Results and Discussion

RESULTS AND DISCUSSION

4.1. DEGRADATION OF ORGANIC SPECIES IN SINGLE SYSTEMS BY FERRATE(VI)

4.1.1. IDA (Iminodiacetic acid)

4.1.1.1. Degradation of IDA species using UV-Vis measurements

4.1.1.1.1. Effect of Fe(VI) Concentration

The degradation of IDA in presence of different concentrations of Fe(VI) was performed at pH~10.0 taking various molar compositions of IDA with Fe(VI) as 2:0.5, 2:1, 2:2, 2:3, 2:5, 2:7 at constant concentration of IDA, i.e., 2.0 x 10^{-4}mol/L. The change in absorbance of the solutions measured as a function of time for a period of 30 mins at 510 nm using UV-Visible Spectrophotometer was recorded as to observe the change in concentration of Fe(VI) and the results obtained were shown in Figure 4.1. The results indicated that a fast initial decrease in concentration of Fe(VI) was observed in the initial stage of Fe(VI) treatment which was further slowed down in the latter stages of time, in particular for the higher molar ratios of IDA to Fe(VI) i.e., for 2:5 and 2:7. Moreover, increasing the concentration of Fe(VI) was caused to enhance the degradation of Fe(VI). This inferred that increasing the concentration of Fe(VI) was caused to increase the decomposition of IDA for a constant initial concentration of IDA. It was further noted that with the increase in Fe(VI) dose, the initial degradation of Fe(VI) was getting faster; beyond the stoichiometric ratio of 2:5, *i.e.*,with the concentration of Fe(VI) as 5.0 x10^{-4} mol/L or more, relatively fast degradation of Fe(VI) took place within 10 mins of contact time after which the concentration of Fe(VI) attained almost a constant value indicating that most of the IDA was degraded within this period. The increase in IDA degradation with increase in Fe(VI) concentration was attributed to the stability of Fe(VI) in aqueous solutions which was governed by factors such as Fe(VI) concentration, temperature of the solution, co-existing ions, pH etc. (Johnson and Sharma, 1999). Previously, it was reported that Fe(VI) was known to be more stable in diluted than in the concentrated solution (Schreyer *et al.*, 1951) and hence, more reactive in the concentrated solutions. Other report demonstrated that a 0.01M potassium ferrate solution decomposed to 79.5% over a period of 2.5 h, while a 0.0019M potassium ferrate solution decreased to only 37.4% after 3 h and 50 min at 25°C (Wagner *et al.*, 1952).

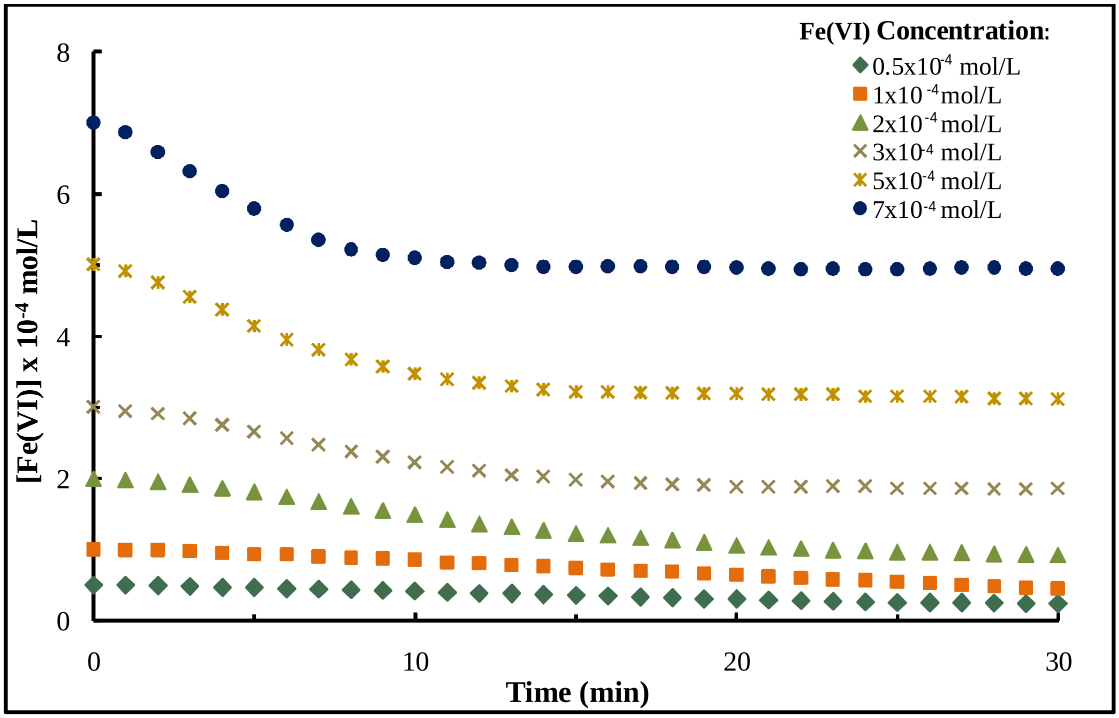


Figure 4.1. *Degradation of Fe(VI) as a function of time for different concentration of Fe(VI) for the constant IDA concentration of 2.0x10^{-4} mol/L at constant pH 10.0.*

4.1.1.1.2. Kinetics of the oxidation of IDA in presence of Fe(VI)

The basic oxidation-reduction reaction involved in the oxidation of IDA by Fe(VI) can perhaps, be written as:

IDA + Fe(VI) à Intermediates à Products + Fe(III) … (4.1)

The rate expression for the reaction of Fe(VI) with IDA can be written as :

$$-\frac{d[Fe(VI)]}{dt} = k \times [Fe(VI)]^m \times [IDA]^n \qquad \ldots(4.2)$$

where [Fe(VI)] and [IDA] are the concentrations of Fe(VI) and IDA respectively; ‘m’ and ‘n’ are their respective order and ‘k’ is the overall reaction rate constant. Kinetic studies were carried out using the data obtained for the amount of Fe(VI) degraded for various molar ratios of IDA to Fe(VI). Further, the above equation (4.2) may be written as:

$$-\frac{d[Fe(VI)]}{dt} = k_1 \times [Fe(VI)]^m \qquad \ldots(4.3)$$

where $k_1 = k[IDA]^n$ …(4.4)

Equation (4.3) was used to deduce the rate kinetics in particular to the reduction of Fe(VI). The change in Fe(VI) concentration data obtained individually for different IDA:Fe(VI) molar ratios were used for the first and second-order rate kinetics (as taking m=1 or 2) and was observed that the results were best fitted to the first order rate kinetics (i.e., m=1) since relatively high value of R^2 was obtained for these systems. Hence it was assumed that the degradation of Fe(VI) in presence of IDA followed the pseudo-first-order rate equation as shown in Figure 4.2.Therefore, using the pseudo-first-order-rate equation, the rate constants were obtained for the degradation of IDA for various concentrations of Fe(VI) at constant molar concentration of IDA. The results obtained were then returned in Table 4.1. It was observed that with the increasing dose of Fe(VI) from $0.5\text{x}10^{-4}$ to $7.0\text{x}10^{-4}$ mol/L, the rate of Fe(VI) degradation or IDA oxidation was increased from $2.76\text{x}10^{-2}$ to $3.92\text{x}10^{-2}$ min^{-1}. These results were in conformity with the fact that Fe(VI) is more degradable at higher concentration for a constant concentration of IDA. Sharma *et al.,* (2006b) also performed kinetics of the oxidation of antibacterial drug sulfamethoxazole (SMX) by Fe(VI) and concluded that the rate law for the oxidation of SMX by Fe(VI) was pseudo-first-order with respect to each reactant as the plot of k_1 values *vs* [SMX] were linear with high correlation coefficient.

Table 4.1. *Pseudo-first-order rate constants for the degradation of Fe(VI) in presence of IDA*

IDA concentration (mol/L)	Fe(VI) Concentration (mol/L)	First order rate constant $k_1 \times 10^{-2}$ (min^{-1})	R^2
2.0×10^{-4}	0.5×10^{-4}	2.76	0.986
2.0×10^{-4}	1.0×10^{-4}	2.30	0.986
2.0×10^{-4}	2.0×10^{-4}	3.22	0.991
2.0×10^{-4}	3.0×10^{-4}	2.99	0.991
2.0×10^{-4}	5.0×10^{-4}	3.91	0.993
2.0×10^{-4}	7.0×10^{-4}	3.92	0.996

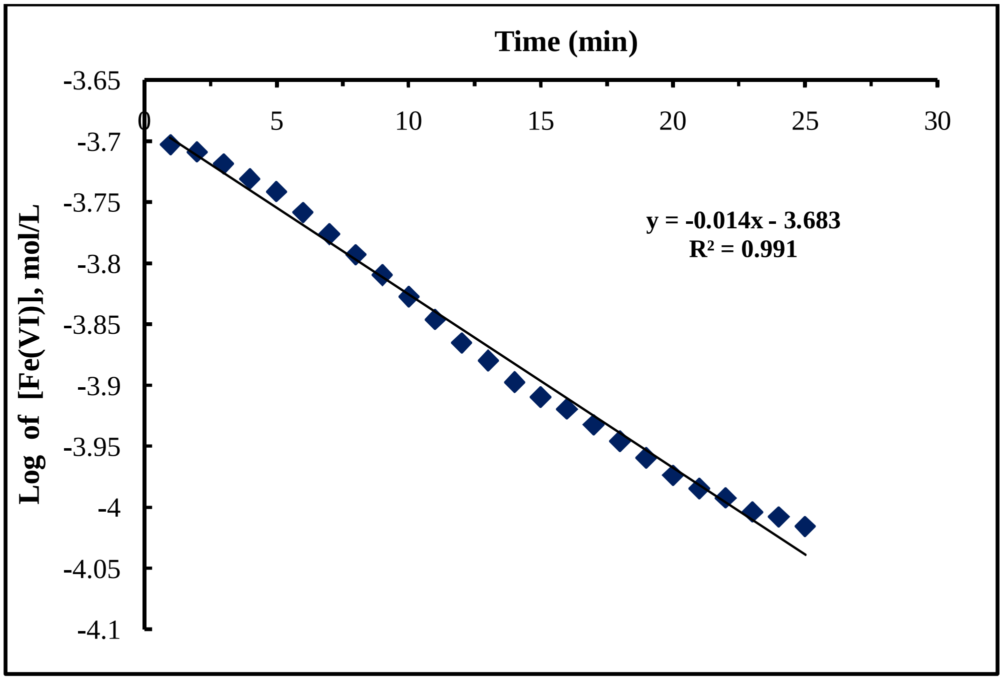


Figure 4.2. *Pseudo First order rate kinetics for Fe(VI) in presence of IDA at pH 10.0 {[Conc. of Fe(VI): 2.0 x 10^{-4} mol/L] [Conc. of IDA: 2.0 x 10^{-4} mol/L]}*

4.1.1.2. Mineralization of IDA species using TOC measurements

The degradation/mineralization of IDA by Fe(VI) was repeated for TOC measurements by treating various molar concentrations of IDA by constant dose of Fe(VI) at different pH values ranging from pH 8.0 to pH 12.0 The treated samples containing different molar ratios of Fe(VI) and IDA (1:0.3 to 1:15) for each pH value and the corresponding blank samples were analyzed for total carbon contents. Based on the TOC data obtained, the percent decomposition of IDA for each sample was calculated. The results obtained were represented graphically in Figure 4.3. The figure indicated that higher percent of IDA was degraded at lower concentrations of IDA using a constant dose of Fe(VI). Quantitatively, IDA was found to be mineralized from 3.25% to 98.02%, respectively, decreasing the concentration of IDA from 15.0 x10^{-4} to 0.3 x10^{-4} mol/L obtained at pH 8.0. indicating that more and more percent of IDA could be degraded at lower IDA concentration for a constant dose of Fe(VI). The results further demonstrated that lower pH values favored the degradation of IDA in solution which is in accordance to the previous studies conducted for the degradation of trichloroethylene by Fe(VI) in which it was degraded maximum at pH 8.0 and decreased further up to pH 11.0. (Graham *et al.,* 2004). The reactivity of the Fe(VI) was gradually increased with decreasing the pH values since the redox potential of Fe(VI) is significantly high at low pH values (Tiwari *et al.,* 2007).

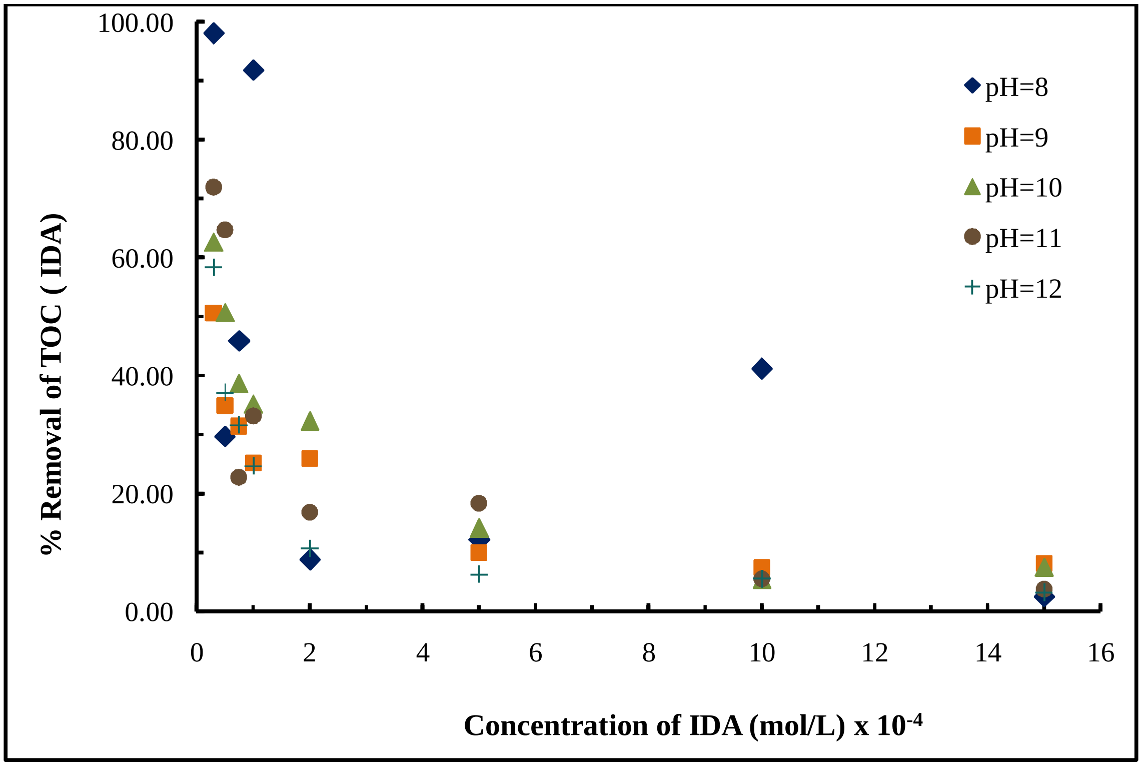


Figure 4.3. *Degradation of IDA as a function of IDA concentration and pH [Initial concentration of Fe(VI): 1.0x10^{-4}mol/L]*

4.1.2. NTA (Nitrilotriacetic acid)

4.1.2.1. Degradation of NTA species using UV-Vis measurements

4.1.2.1.1. Effect of Fe(VI) Concentration

The degradation of NTA in a single system in presence of Fe(VI) was investigated by taking various molar ratios of NTA to Fe(VI) i.e., 1: 0.25 to 1: 3.5 keeping initial concentration of NTA constant at 2.0 x10^{-4} mol/L and at constant pH 10.0. The UV-Visible data was recorded at 510 nm for each solution to obtain the change in concentration of Fe(VI) with time. The results are shown graphically in Figure 4.4. It was noted that increasing the concentration of Fe(VI), initial fast degradation of Fe(VI) occurred; clearly suggesting tha tmaximum decomposition of NTA took place during the initial period of contact. Within initial 10 to 15 mins, very fast degradation ofFe(VI) had taken place and thereafter, it was slowed down attaining more or less constant value.

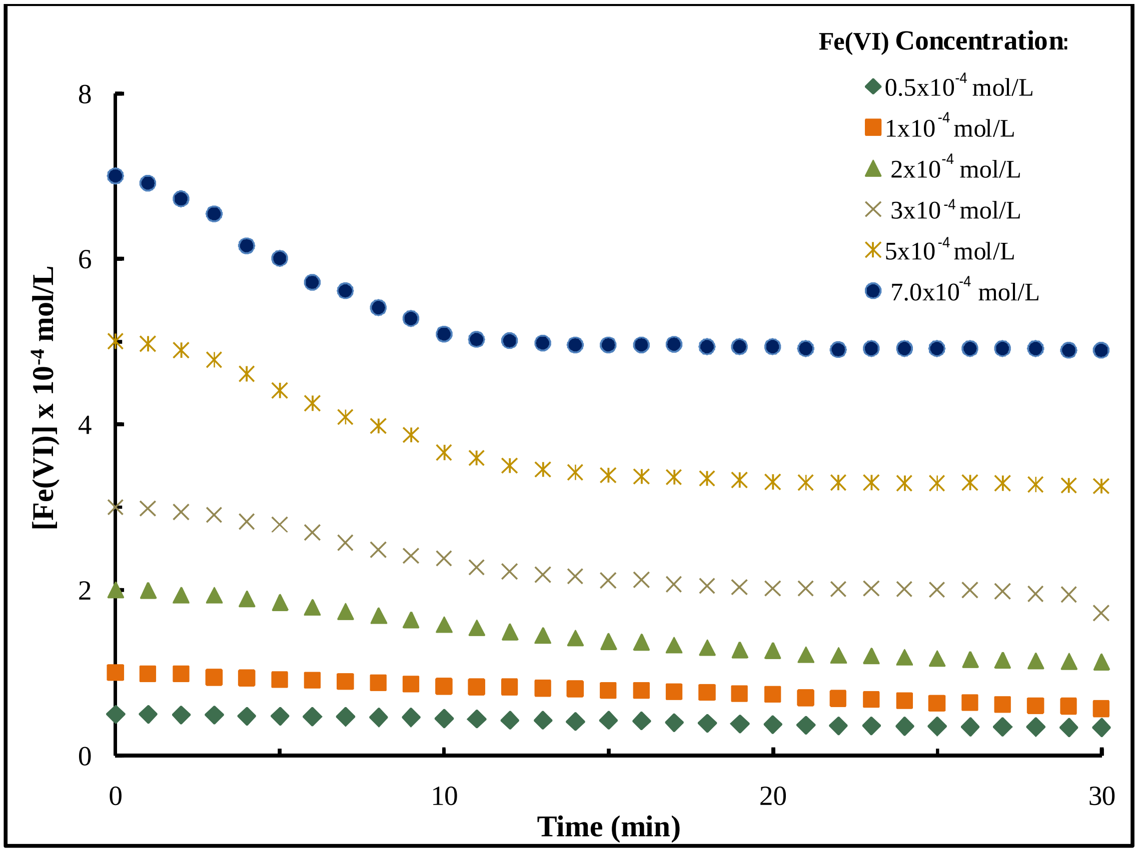


Figure 4.4. *Degradation of Fe(VI) as a function of time for different concentration of Fe(VI) for the constant NTA concentration of $2.0x10^{-4}$ mol/L at constant pH 10.0.*

4.1.2.1.2. Kinetics of the oxidation of NTA in presence of Fe(VI)

Similar to the previous system under study i.e., IDA, the basic oxidation-reduction reaction involved in the oxidation of NTA by Fe(VI) may be again represented as :

NTA + Fe(VI) à Intermediates à Products + Fe(III) … (4.5)

Kinetic studies were again carried out using the data obtained for the amount of Fe(VI) degraded for various molar ratios of NTA to Fe(VI) using the rate equation below:

$$-\frac{d[Fe(VI)]}{dt} = k_1 \times [Fe(VI)]^m \qquad \ldots (4.6)$$

$$\text{where } k_1 = k[NTA]^n \qquad \ldots (4.7)$$

Taking m=1 or 2 in equation (4.6), pseudo-first and pseudo-second-order rate kinetics were obtained for all these systems studied. The results were best fitted to the pseudo-first-order rate kinetics (i.e., m=1) rather the pseudo-second-order rate kinetics since relatively high correlation coefficient was obtained for this. These results indicated that the oxidation of NTA by Fe(VI) followed pseudo-first-order rate kinetics. The obtained pseudo-first-order-rate kinetics for the 1:1 molar ratio of Fe(VI) and NTA at pH 10.0 was shown in Figure 4.5. The pseudo- first-order-rate constants were obtained for these systems and returned in table 4.2. Quantitatively, increasing the concentration of Fe(VI) from 0.5×10^{-4} to 7.0×10^{-4} mol/L, the pseudo-first-order rate constant for Fe(VI) degradation or IDA oxidation was increased from 1.38×10^{-2} to 3.45×10^{-2} min^{-1}. These results are in line with the IDA degradation by Fe(VI) obtained previously. Pseudo-first-order-rate constant with respect to the concentration of Fe(VI) was similarly obtained for the oxidation of cyanide by Fe(VI) and reported to be 6.8015×10^{-3} sec^{-1}(Tiwari *et al.*, 2006).

Table 4.2. *Pseudo-first-order rate constants for the degradation of Fe(VI) in presence of NTA*

NTA concentration (mol/L)	Fe(VI) Concentration (mol/L)	First order rate constant $k_1 \times 10^{-2}$ (min^{-1})	R^2
2.0×10^{-4}	0.5×10^{-4}	1.382	0.983
2.0×10^{-4}	1.0×10^{-4}	1.612	0.981
2.0×10^{-4}	2.0×10^{-4}	2.303	0.986
2.0×10^{-4}	3.0×10^{-4}	2.533	0.987
2.0×10^{-4}	5.0×10^{-4}	2.994	0.980
2.0×10^{-4}	7.0×10^{-4}	3.455	0.989

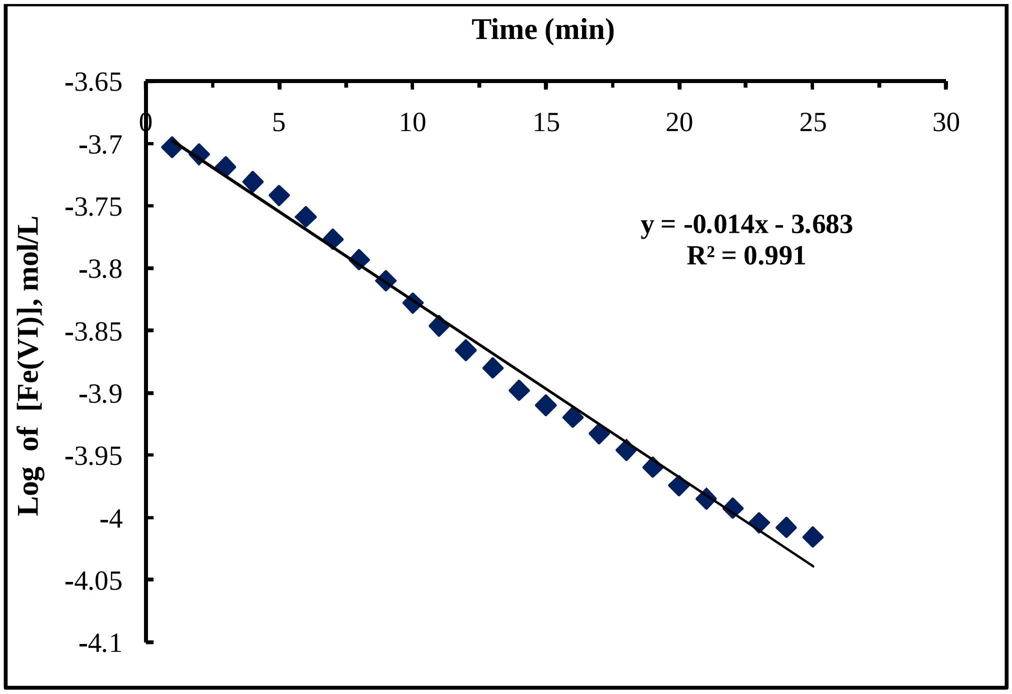


Figure 4.5. *Pseudo-first-order rate kinetics for Fe(VI) in presence of NTA at pH 10.0 {[Conc. of Fe(VI): 2.0 x 10^{-4} mol/L] [Conc. of NTA: 2.0 x 10^{-4} mol/L]}*

4.1.2.2. Mineralization of NTA using TOC measurements

The degradation/mineralization of NTA by Fe(VI) was further evaluated for the treated samples of the varied molar concentrations of NTA at pH~10.0. The TOC data obtained were used to calculate the percent removal of TOC for each varied molar ratio of Fe(VI) and NTA (1:0.3 to 1:7) keeping initial constant dose of Fe(VI) as 1.0x10^{-4} mol/L. The results shown in figure 4.6 clearly indicated that the increase in concentration of NTA caused for decrease in percent decomposition of NTA studied at constant dose of Fe(VI). Quantitatively, NTA was found to be mineralized from 1.69% to 49.75%, respectively, decreasing the concentration of NTA from 15.0 to 0.3 mol/L at pH~10.0. The results are in line with the IDA mineralization by Fe(VI) since more and more IDA was degraded at lower molar ratios of IDA to Fe(VI).

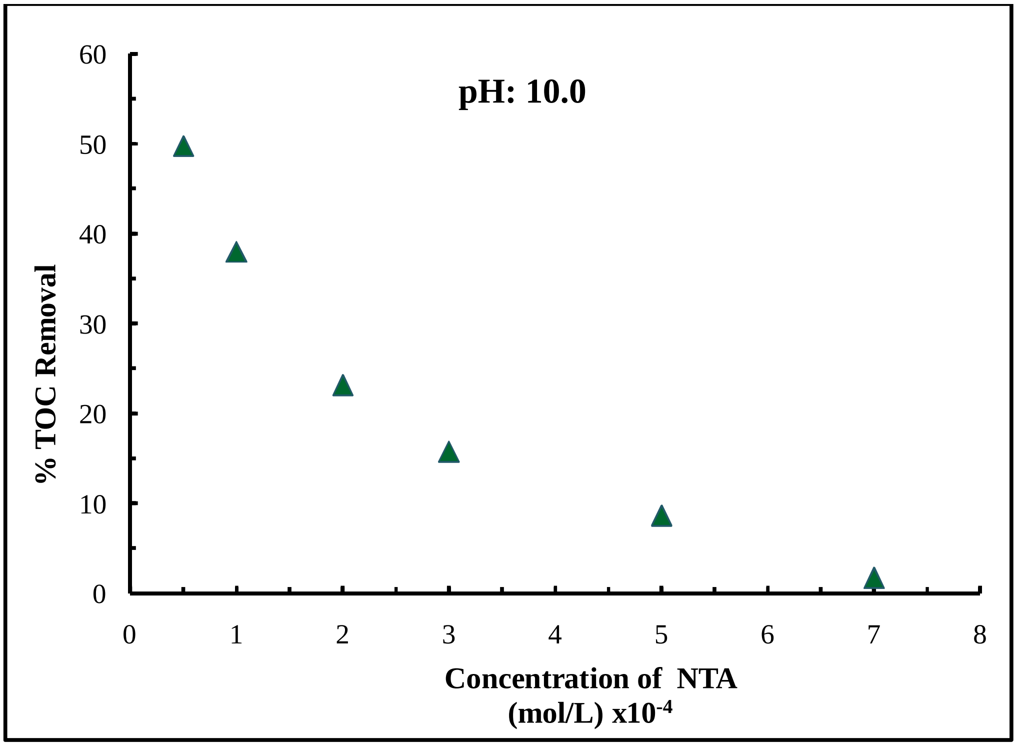


Figure 4.6. *Degradation of NTA as a function of NTA concentration at constant pH:10.0 [Initial conc. of Fe(VI):1.0x10^{-4} mol/L].*

4.1.3. EDTA (Ethylenediaminetetraacetic acid)

4.1.3.1. Degradation of EDTA species using UV-Visible measurements

4.1.3.1.1. Effect of Fe(VI) Concentration

The degradation of EDTA by the varied dose of Fe(VI) was investigated at constant pH 10.0. The molar concentration of EDTA was taken as constant, 2.0 x 10^{-4}mol/L and the doses of Fe(VI) was varied from (0.5 to 7.0) x10^{-4}mol/L. The degradation of Fe(VI) was recorded at 510 nm for a period of 30 min using UV-Visible spectrophotometer. The results obtained were demonstrated in Figure 4.7. It was again observed that the increase in concentration of Fe(VI) resulted in more and more degradation of Fe(VI) which has, possibly, caused for higher decomposition of EDTA. Fast initial degradation of Fe(VI) was observed with the increase in Fe(VI) concentration and reached to a constant value within *Ca.*10 to 15 min of contact time for higher doses of Fe(VI). Previous studies showed that the Fe(VI) efficiently oxidized various synthetic organic compounds, *viz.*, benzene, chlorobenzene, allylbenzene and phenol etc. (Bielski *et al.*,1994). Moreover, the fast and efficient degradation of these pollutants by Fe(VI) was further increased with increase in Fe(VI) dose.

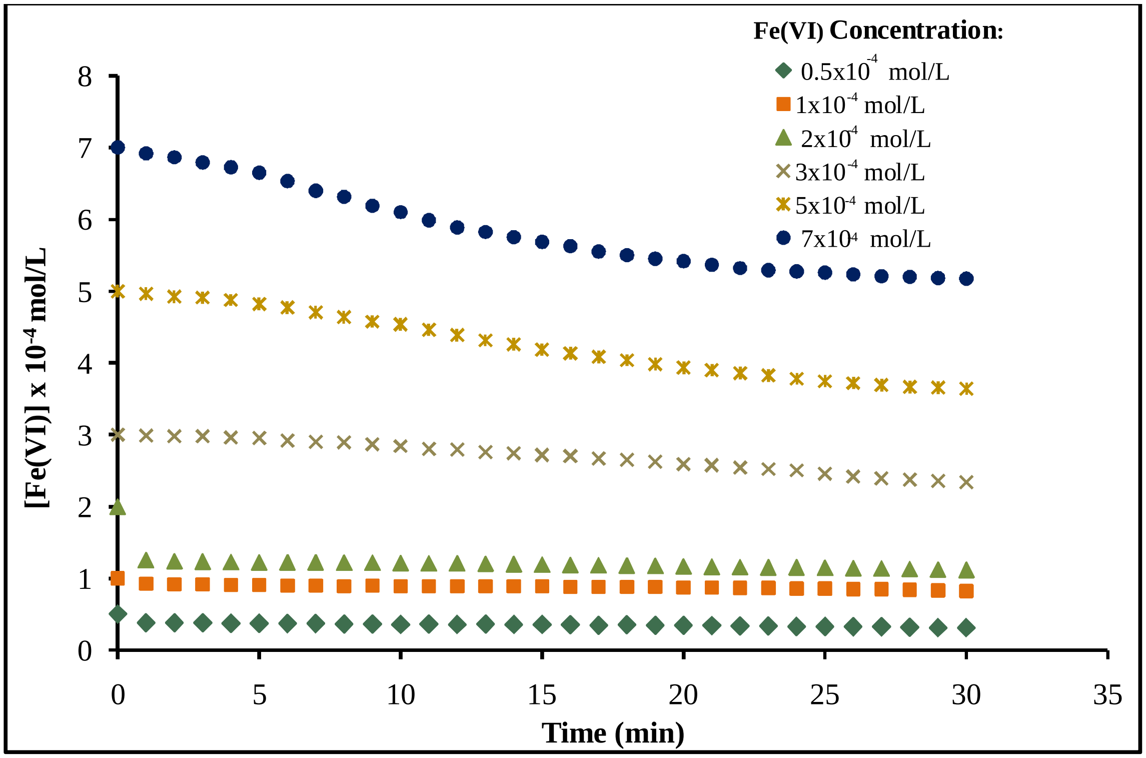


Figure 4.7. *Degradation of Fe(VI) as a function of time for different concentration of Fe(VI) at constant EDTA concentration of 2.0x10*$^{-4}$ *mol/L and at constant pH: 10.0.*

4.1.3.1.2. Kinetics of the oxidation of EDTA in presence of Fe(VI)

Similar to IDA and NTA, the degradation of the EDTA by Fe(VI) could be demonstrated as:

$$\text{EDTA} + \text{Fe(VI)} \rightarrow \text{Intermediates} \rightarrow \text{Products} + \text{Fe(III)} \qquad \text{.... (4.8)}$$

And the rate law derived at:

$$-\frac{d[Fe(VI)]}{dt} = k_1 \times [Fe(VI)]^m [EDTA]^n \qquad \text{.... (4.9)}$$

$$\text{where } k_1 = k[EDTA]^n \qquad \text{.... (4.10)}$$

[Fe(VI)] and [EDTA] are the concentrations of Fe(VI) and EDTA respectively; m and n are their respective order and k is the overall reaction rate constant. The kinetic interpretations of the UV-Visible data obtained for the oxidation of EDTA in presence of Fe(VI) indicated that the reaction followed pseudo-first-order rate law at least in the degradation of Fe(VI). Figure 4.8represents the Pseudo first order rate law for the reduction of Fe(VI) with EDTA for the molar ratio of Fe(VI) to EDTA as 1:1. The pseudo-first-order rate constants were obtained for the different doses of Fe(VI) and were tabulated in Table 4.3. It was observed that the rate of decomposition of Fe(VI) was enhanced with increasing the concentration of Fe(VI). This indicated that more and more degradation of EDTA occurred at higher doses of Fe(VI). Quantitatively, increasing Fe(VI) doses from 0.5 $x10^{-4}$ to 7.0 $x10^{-4}$ mol/L, the corresponding rate constant values were increased from 4.61 $x10^{-3}$ to 13.82 $x10^{-3}$ min^{-1}. These results were in accordance with the other pollutants, *viz.*, IDA and NTA as studied separately previously. It was further observed that the rate constants followed the order, IDA>NTA>EDTA which indicated that EDTA was relatively more stable than NTA and IDA.

Table 4.3. *Pseudo-first-order rate constants for the degradation of Fe(VI) in presence of EDTA*

EDTA concentration (mol/L)	Fe(VI) Concentration (mol/L)	First-order-rate constant k_1 x 10^{-3} (min^{-1})	R^2
2.0 x 10^{-4}	0.5 x 10^{-4}	4.61	0.959
2.0 x 10^{-4}	1.0 x 10^{-4}	2.30	0.971
2.0 x 10^{-4}	2.0 x 10^{-4}	2.30	0.982
2.0 x 10^{-4}	3.0 x 10^{-4}	6.91	0.986
2.0 x 10^{-4}	5.0 x 10^{-4}	11.51	0.989
2.0 x 10^{-4}	7.0 x 10^{-4}	13.82	0.983

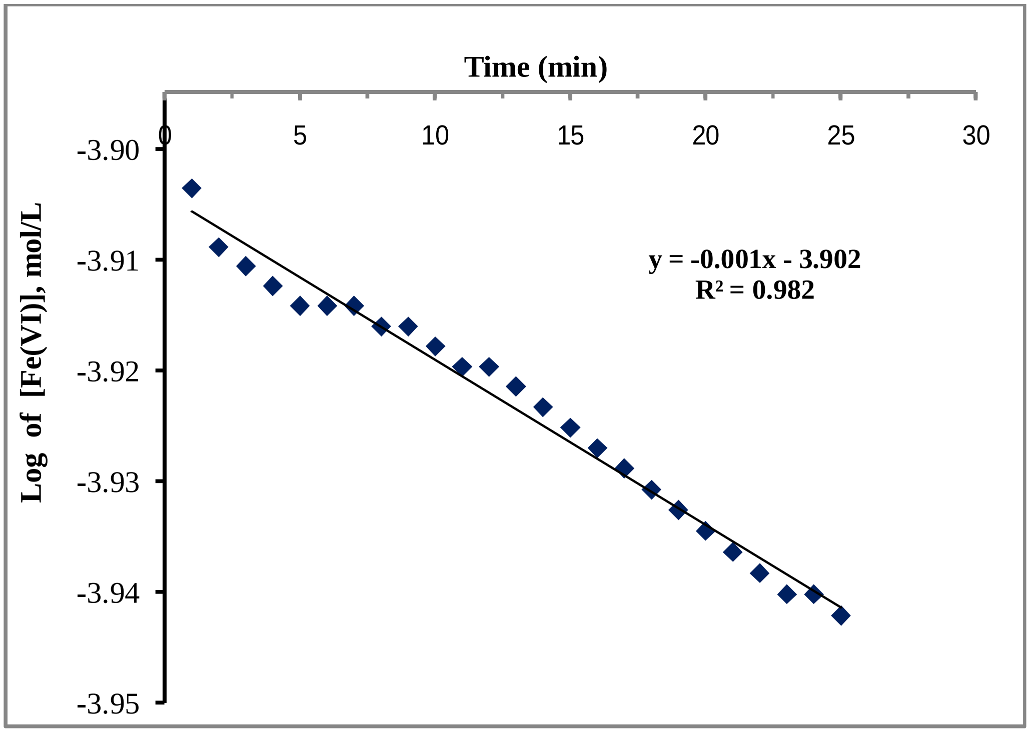


Figure 4.8. *Pseudo-first-order rate kinetics for Fe(VI) in presence of EDTA at pH 10.0. {[Conc. of Fe(VI): 2.0 x 10^{-4}mol/L][Conc. of EDTA: 2.0 x 10^{-4} mol/L]}*

4.1.3.2. Mineralization of EDTA using TOC measurements

The study of EDTA degradation/mineralization by Fe(VI) was investigated by using the TOC measurements. The various concentrations of EDTA (i.e., from 0.3 x10^{-4} to 7 x10^{-4} mol/L) was treated with a constants dose of Fe(VI), 1.0x10^{-4} mol/L a ta constant pH 10.0. The obtained results were represented graphically in Figure 4.9. The figure clearly indicated that higher percent removal of EDTA occurred at lower concentration of EDTA. Decreasing the concentration of EDTA from 15.0 x10^{-4} to 0.3 x10^{-4} mol/L resulted in the increase in percent removal of EDTA from 3.08 to 48.13% at pH 10.0. The mineralization of the IDA, NTA and EDTA by Fe(VI) treatment followed the order IDA>NTA>EDTA. These results were in accordance to the pseudo-first-order rate constant values obtained for the degradation of Fe(VI) in presence of IDA, NTA or EDTA.

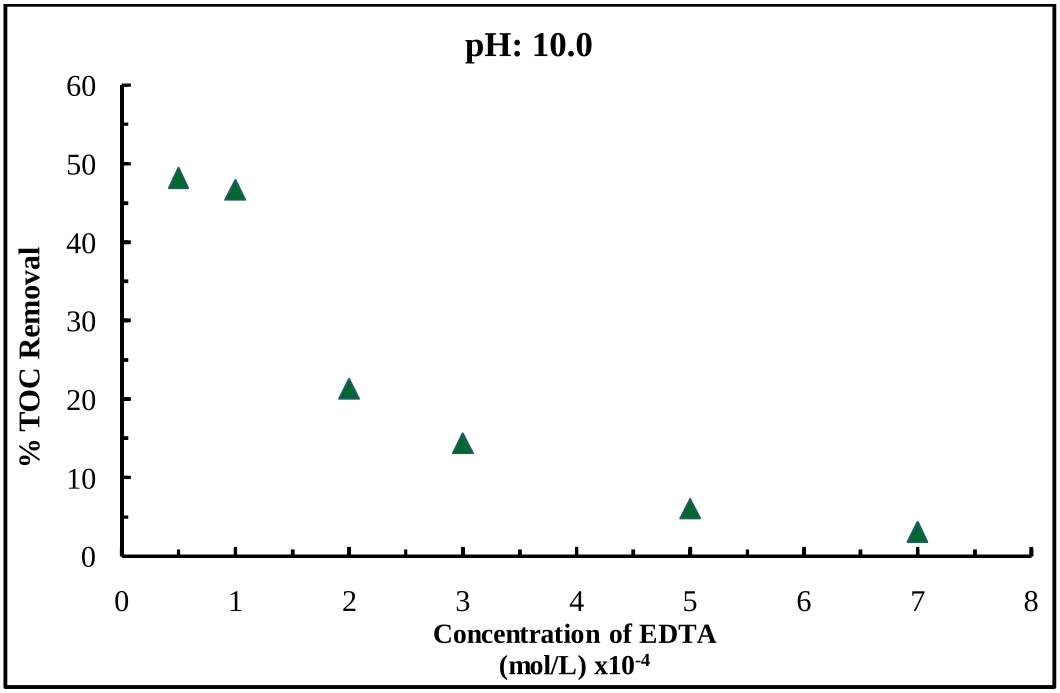


Figure 4.9. *Degradation of EDTA as a function of EDTA concentration at constant pH:10.0 [Initial conc. of Fe(VI)]: $1.0x10^{-4}$ mol/L]*

4.2. DEGRADATION OF METAL(II)-ORGANIC COMPLEXED SYSTEMS BY FERRATE(VI)

4.2.1. Cu(II)-IDA System

4.2.1.1. Decomplexation and degradation of Cu(II)-IDA complex species

4.2.1.1.1. Effect of Cu(II)-IDA Concentration

The decomplexation and degradation of Cu(II)-IDA complexe species was investigated by the change in Fe(VI) concentration obtained by the UV-Vis measurement recoded at 510 nm of wavelength. The study was conducted as a function of Cu(II)-IDA concentration varied from 0.3 mmol/L to 15.0 mmol/L at a constant dose of Fe(VI), 1.0 mmol/L. In other words, the moler ratio of Cu(II)-IDA with Fe(VI) was varied from 0.3:1 to 15:1. The complex species were also treated at different pH values i.e., from pH 8.0 to 12.0. The UV-Visible data obtained were shown graphically in figures 4.10(a) to 4.10(c) respectively for pH 9.0, 10.0, and 11.0. These figures clearly demonstrated that a fast decrease/removal of Fe(VI) occurred during the initial period of time which slowed down with the latter stage of time and attained almost a constant value just after *Ca*. 15-20 mins of contact time. It was further noted that increasing the molar concentration of Cu(II)-IDA generally caused to enhance the decomplexation/degradation of Cu(II)-IDA species in solutions as more and more Fe(VI) was removed with an enhanced rate. The initial fast degradation of the complex species was even more pronounced at higher concentration of Cu(II)-IDA as indicated by the removal rate of Fe(VI). At pH 9, Fe(VI) was completely decomposed in presence of 15.0 mmol/L of Cu(II)-IDA just within 2 mins of contact time whereas, the similar complete removal of Fe(VI) was achieved within 6 and 13 mins of contact time, obtained respectively for 10.0 mmol/L and 5.0 mmol/L $x10^{-3}$ mol/L of Cu(II)-IDA. Similarly, at pH 10.0, the complete removal of Fe(VI) was observed within 11 mins for 15.0 mmol/L of Cu(II)-IDA concentration. In other words, increasing the pH gradually caused to decrease the reactivity of the Fe(VI) or the rate of decomposition of Fe(VI) was decreased significantly at higher pH values. These observations clearly suggested that increasing the pollutant concentration, could effectively be treated with the regulated dose of Fe(VI). It was previously reported that increasing the concentration of Cu(II)-CN or Ni(II)-CN caused in rapid removal of Fe(VI) (Lee *et al.,* 2009) or even the fast degradation of Cu(I)-CN complexed species in aqueous solutions (Sharma *et al.,* 2008b).

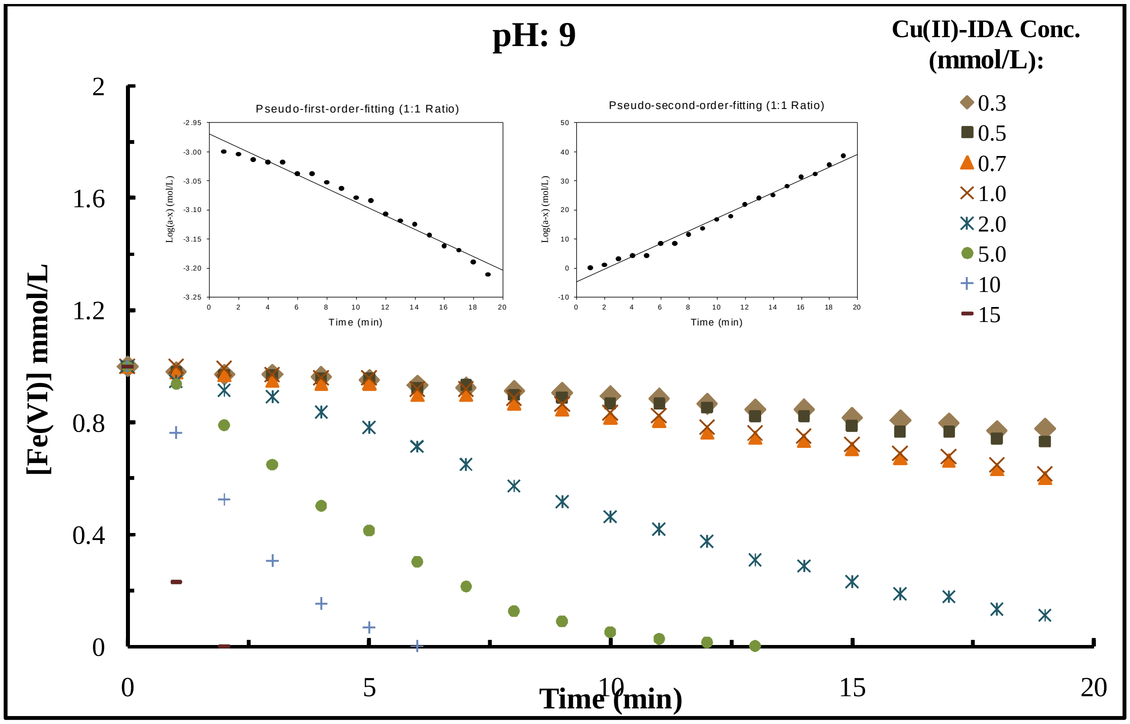


Figure 4.10(a). *Degradation of Fe(VI) as a function of time for various concentrations of Cu(II)-IDA at pH 9.0.*

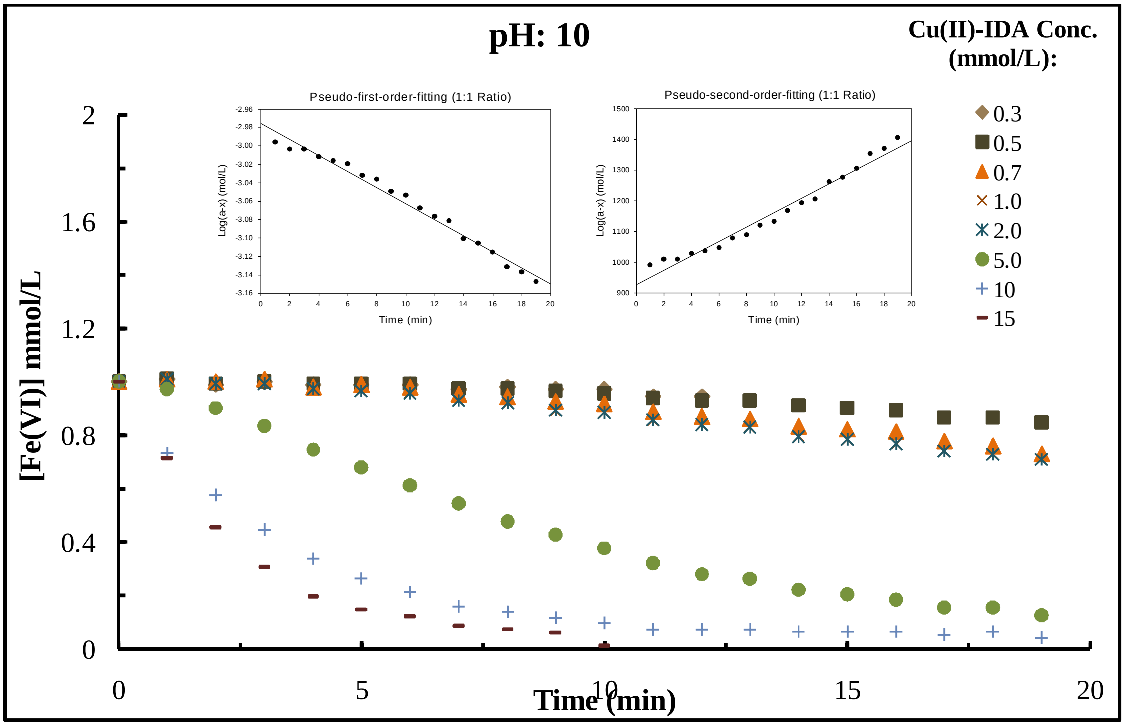


Figure 4.10(b). *Degradation of Fe(VI) as a function of time for various concentrations of Cu(II)-IDA at pH 10.0.*

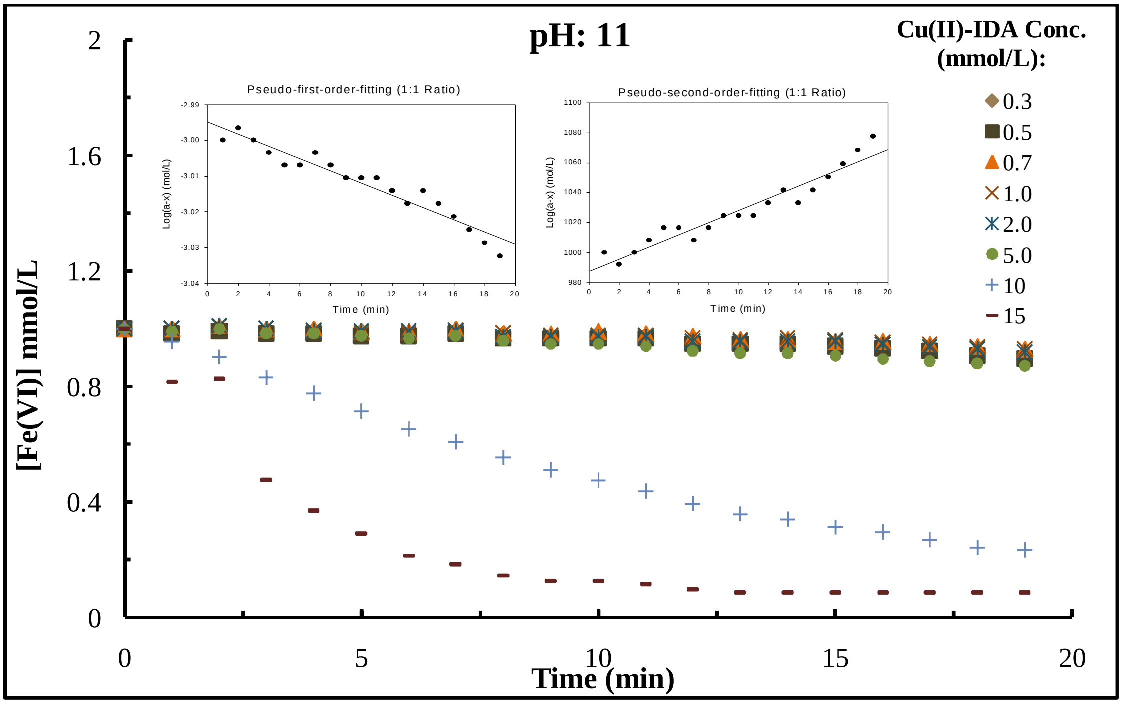


Figure 4.10(c). *Degradation of Fe(VI) as a function of time for various concentrations of Cu(II)-IDA at pH 11.0.*

4.2.1.1.2. Kinetics of Cu(II)-IDA decomplexation/degradation

Further, the kinetics of the removal of Fe(VI) was carried out in the oxidation of Cu(II)-IDA using the time dependence data collected at different pH values and molar ratios of Fe(VI) to Cu(II)-IDA. The ferrate(VI) is readily reduced into Fe(III) through the reductive pathways as suggested elsewhere (Zhang *et al.*, 2012):

$$2FeO_4^{2-} + 3H_2O \rightarrow 2Fe(OH)_3 + 5\,[O] \qquad \ldots (4.11)$$

$$[O] + H_2O \rightarrow 2\,{}^{\bullet}OH \qquad \ldots (4.12)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \qquad \ldots (4.13)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \ldots (4.14)$$

The generated hydroxyl free radical possessed with strong oxidizing capacity. However, the reactions of Fe(VI) with several organic/inorganic pollutants in aqueous medium were found to be complicated to demonstrate; since either a direct oxidation by Fe(VI) took place or by the newly generated hydroxyl free radicals initiated the oxidation process. The simple kinetics in degradation of Cu(II)-IDA was suggested by the change in Fe(VI) concentration using the UV-Vis data collected at 510 nm wave length. Therefore, the basic equation for degradation of Fe(VI) could be regarded as:

$$\text{Fe(VI)} + \text{Cu(II)-IDA} \rightarrow \text{Fe(III)} + \text{Oxidized Products} + CO_2 + N_2 \quad \ldots (4.15)$$

It was assumed that partly/fully, the decomplexed IDA was mineralized as enabled with total organic carbon analysis and was partly not degraded or some intermediates formed. Moreover, the term of self-decomposition of ferrate(VI) which was significant at relatively low pH values (Tiwari *et al.*, 2007; Lee *et al.*, 2004) was eventually excluded since the necessary correction was done using the blank data collected at that pH and keeping the other physico-chemical conditions identical. The rate of decomposition of ferrate(VI) could be expressed as:

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Cu(II)-IDA]^n \quad \ldots (4.16)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)]^m \quad \ldots (4.17)$$

$$k_1 = k\,[\text{Cu(II)-IDA}]^n \quad \ldots (4.18)$$

[Fe(VI)] and [M(II)-IDA] are the concentrations of ferrate(VI) and Cu(II)-IDA in solution, respectively. ‘k’ is the overall rate constant to each reactant. ‘m’ and ‘n’ are the order of reaction for each species which was estimated with the empirical fitting of the ferrate (VI) concentration and Cu(II)-IDA concentration data. In order to optimize the value of ‘m’ the data was plotted between the Log(a-x) *vs*‘t’ and 1/(a-x) *vs*‘t’ as to enable the pseudo-first order and pseudo-second order rate laws. The term (a-x) is the concentration of Fe(VI) remained in bulk solution at time ‘t’. The fitting results of pseudo-first and pseudo-second order equations are represented in figures 4.10(a), 4.10(b) and 4.10(c)(inset in figures) respectively fitted at pH 9.0, 10.0 and 11.0 having the 1:1 Fe(VI) and Cu(II)-IDA molar stoichiometry. The data was computed for all the studied molar ratios and at different pH values which were then returned in Table 4.4. Data clearly indicated that decreasing the pH from 11.0 to 8.0 apparently caused significantly to increase the rate of Fe(VI) removal, at least in presence of Cu(II)-IDA species (*cf* Table 4.4). More quantitatively, decreasing the pH from 11.0 to 8.0, the rate constant was increased, respectively from 0.390 x10^{-2} to 3.43 x10^{-2} min^{-1} (for pseudo-first-order) and from 4.05 to 48.09 L/mol/min (for pseudo-second-order) at the 1:1 molar ratios of Fe(VI) to Cu(II)-IDA. The rapid and fast removal of ferrate(VI) at lower pH values was possibly due to the higher redox potential of Fe(VI) at lower pH values (Sharma *et al.,* 2002; Jiang and Llyod, 2002). It was also noted that, apparently, at pH values 12.0, the rate of decomposition of Fe(VI) was almost independent with increasing the Cu(II)-IDA concentration (data not included). Moreover, the removal rate constant of Fe(VI) was also found to be significantly low at pH 12.0. This could be explicable with the fact that at very high pH conditions the reactivity of Fe(VI) was decreased greatly; whereas the stability of Fe(VI) was increased significantly at this high pH value (Tiwari *et al.,* 2005; Sharma *et al.,* 2002; Jiang and Llyod, 2002). Further, the closure scrutiny of the data showed that pseudo-first-order or pseudo-second-rate constant fitting was reasonably well to both the equations and apparently comparable to each other. It was difficult to pinpoint the possible order of Fe(VI) removal in respect of Fe(VI) removal.

Table 4.4. *Pseudo-first and Pseudo-second order rate constants obtained for the removal of ferrate(VI) using various concentration of Cu(II)-IDA at different pH conditions.*

[Cu (II)-IDA] (mmol/L	Pseudo-first-order rate constant (x10^{-2}) (1/min)								Pseudo-second-order rate constant (L/mol/min)							
	pH 8.0		pH 9.0		pH 10.0		pH 11.0		pH 8.0		pH 9.0		pH 10.0		pH 11.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.3	2.85	0.993	1.38	0.979	0.530	0.841	0.530	0.888	38.012	0.997	15.86	0.971	3.98	0.768	5.585	0.880
0.5	2.39	0.981	1.70	0.972	0.944	0.947	0.480	0.884	29.70	0.991	19.93	0.962	10.06	0.939	5.143	0.877
0.7	5.23	0.996	2.69	0.976	1.773	0.959	0.410	0.907	87.36	0.994	34.51	0.955	20.26	0.943	4.177	0.903
1.0	3.43	0.991	2.69	0.976	2.004	0.983	0.390	0.928	48.09	0.996	33.80	0.955	23.49	0.972	4.047	0.924
2.0	7.58	0.980	11.98	0.965	2.004	0.983	0.460	0.949	135.02	0.994	146.96	0.932	23.49	0.972	4.811	0.946
5.0	15.57	0.978	38.16	0.952	11.607	0.997	0.760	0.977	179.74	0.986	344.53	0.974	357.90	30.922	8.496	0.980
10.0	12.92	0.877	60.78	0.980	14.76	0.914	8.110	0.999	260.97	0.932	1710.8	0.887	1131.8	0.953	182.3	0.965
15.0	24.92	0.937	-	-	36.29	0.891	12.51	0.833	424.05	0.976	-	-	1880.0	0.970	852.2	0.982

Further, using these rate constant values the overall rate constant ‘k’ was estimated using the k_1 values (obtained by pseudo-first-order rate constant values as well the pseudo-second-order rate constant). It was observed, for m=1 (i.e., pseudo-first-order rate constants) the obtained rate constant values (k_1) were fitted well since a good linearity was obtained while plotting between k_1 *vs* [Cu(II)-IDA] (*cf*Figure 4.11). Further, the fitting was done for the n=2 i.e., plotting the k_1 *vs* $[\text{Cu(II)-IDA}]^2$, but the fitting was significantly low as R^2 was very low (data and figure not included) and hence, it was apparently ruled out. Therefore, using the pseudo-first-order rate constant values, the overall rate constant values along with the R^2 values were estimated at different pH values and returned in Table 4.5. In general, increasing the pH, the overall rate constant was decreased and attained a minimum value at pH 11.0. This was in accordance to the reactivity of the ferrate(VI) in solution since the protonated ferrate species ($HFeO_4^- \leftrightarrow H^+ + FeO_4^{2}$; $pK_a^2=7.3$) possessed with larger spin density than the deprotonated species (Ohta *et al.*, 2001; Sharma *et al.*, 2004). It was also clearly demonstrated that 1:1 stoichiometry occurred in the decomplexation/degradation of Cu(II)-IDA with ferrate(VI).

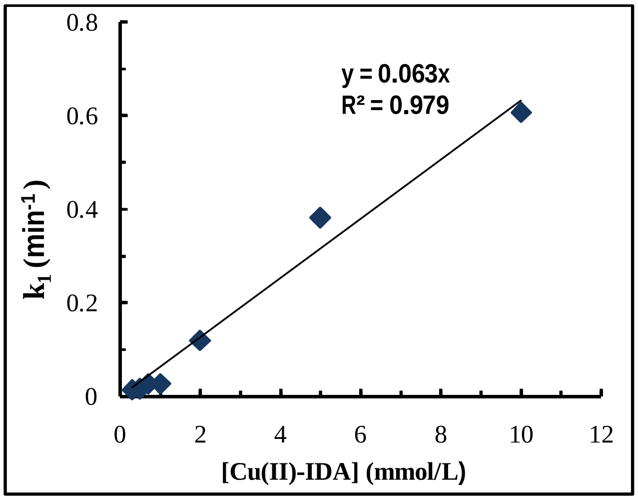


Figure 4.11. *Fitting of pseudo-first-order rate constant values for the degradation of Fe(VI) in presence of different concentrations of Cu(II)-IDA at pH 9.0.*

Table 4.5. *Overall rate constant in the decomplexation /degradation of Cu(II)-IDA by ferrate(VI) at different pH conditions*

pH	**Cu(II)-IDA System**	
	k(L/mol/min)	**R^2**
8.0	32.30	0.950
9.0	63.00	0.979
10.0	16.30	0.919
11.0	7.70	0.922

4.2.1.2. Mineralization of IDA

The ferrate(VI) treatment was supposed to decomplex the complexed species in the first step followed by the oxidation of degradable impurities i.e., IDA and likely to mineralize it. Therefore, the mineralization of IDA in the Cu(II)-IDA samples as treated with Fe(VI) was obtained by using the TOC analytical data. The total organic carbon data obtained for various stoichiometric ratios treated at various pH conditions i.e., pH 8.0 to 12.0 were tabulated in table 4.6 and graphically represented in figure 4.12. The data indicated that higher percent of IDA was degraded at lower concentrations of IDA using a constant dose of Fe(VI). Decreasing the concentration of Cu(II)-IDA from 15.0 to 0.30 mmol/L the corresponding increase in percent removal of TOC was found to be from 3.11% to 46.68% at pH 8.0. These results were in a line to demonstrate that more and more percent IDA was degraded at lower IDA concentration for a constant dose of Fe(VI). Further, it was again reaffirmed that lower pH values favored the degradation of IDA in solution. Same observations were recorded for IDA in the single system and also for trichloroethylene which was degraded maximum in presence of Fe(VI) at pH 8.0 and decreased further up to pH 11.0 (Graham *et al.,* 2004).

Table 4.6. *Removal of IDA from Cu(II)-IDA complex species by Fe(VI) at different pH values*

pH	% Mineralization of IDA using Ferrate(VI)								
	Fe(VI) : [Cu(II)-IDA] [Initial conc. of Fe(VI) : 1.0 mmol/L]								
	1:0.3	**1:0.5**	**1:0.7**	**1:01**	**1:02**	**1:05**	**1:10**	**1:15**	**0**
8	46.68	24.60	22.07	17.29	12.16	5.16	5.24	3.11	
9	44.16	33.22	27.28	24.07	12.65	5.35	12.6	3.50	
10	37.23	32.89	26.79	21.22	14.25	7.00	4.47	2.01	
11	21.47	11.64	9.96	7.81	7.96	4.78	7.01	4.07	
12	10.29	8.73	7.69	5.03	4.37	5.15	2.00	1.91	

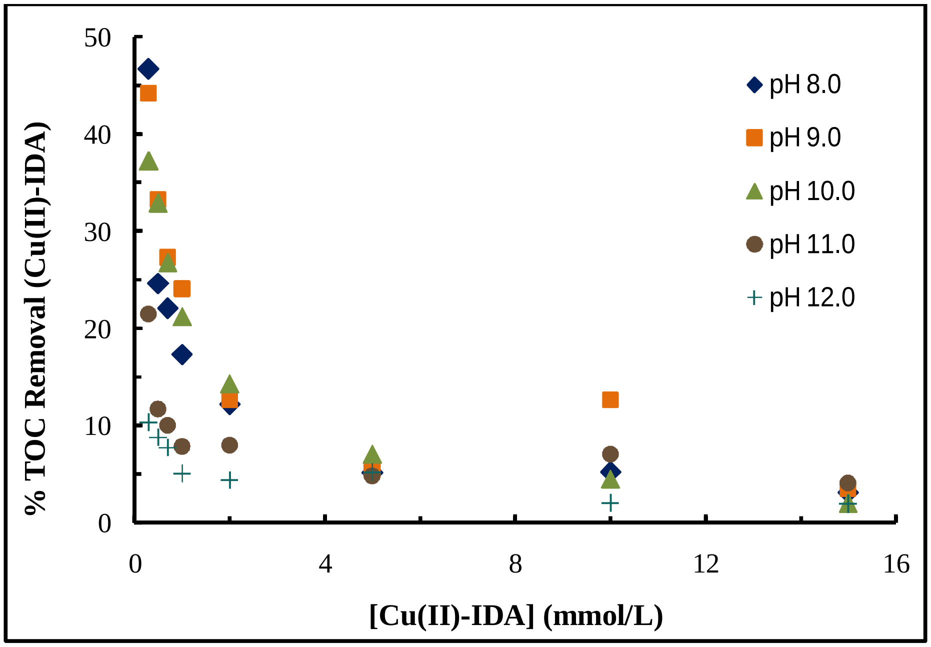


Figure 4.12. *Degradation of IDA for different concentrations of Cu(II)-IDA treated with Fe(VI):1.0 mmol/L at different pH values.*

4.2.1.3. Simultaneous removal of Cu(II)

The additional advantage of the ferrate(VI) treatment was a simultaneous removal of non-degradable metallic impurities by the coagulation/flocculation or even by the adsorption pathways occurred with the reduced ferrate(VI) into Fe(III) which was reasonably an excellent coagulant (Sharma *et al.*, 2008b; Potts and Churchwell, 1994). Hence, the study was extended for the simultaneous removal of Cu(II) from the Fe(VI) treated samples. The removal of Cu(II) was obtained; analyzing the treated and filtered samples at the treated pH as well at the higher pH i.e., pH 12.0 by raising the pH of the treated solution at pH 12.0 using conc. NaOH solution. The percent removal of Cu(II) for different concentrations of Cu(II)-IDA and at different pH values was shown in Table 4.7 and also presented graphically in Figure 4.13. This 3D figure obtained for various concentrations of Cu(II)-IDA showed that partial removal of these metal ions occurred at the lower pH values, however, very high percent removal of Cu(II) was obtained when the treated sample pH was raised to pH 12.0.

These results clearly indicated that the Cu(II)-IDA species treated at various pH values were decomplexed completely; but the mineralization of IDA occurred partly. However, the decomplexed Cu(II) was coagulated significantly at higher pH values since more than 90% of Cu(II) was removed at pH 12.0. Previous studies also indicated that a significant percent of Cu(II) or Ni(II) was removed simultaneously when treated with Fe(VI) at different pH values (Lee and Tiwari, 2009). Moreover, the Cu(I)-cyanide was treated with Fe(VI) and the increasing dose of Fe(VI) was enabled to remove Cu(II) completely and simultaneously by reduced Fe(III) (Sharma *et al.,* 2005a).

Table 4.7. *Percent removal of Cu(II) by Fe(VI) treatment of Cu(II)-IDA at different molar ratios of Fe(VI) to Cu(II)-IDA and at different pH conditions [Initial concentration of Fe(VI): 1.0 mmol/L]*

Fe(VI): Cu(II)-IDA	% Removal of Cu(II) by Fe(VI)								
	pH 8	pH raised to 12	pH 9	pH raised to 12	pH 10	pH raised to 12	pH 11	pH raised to 12	pH12
1:0.3	3.25	94.81	6.68	93.77	19.33	92.02	50.85	90.48	92.02
1:0.5	4.06	94.58	6.54	96.11	4.88	92.89	20.94	93.71	95.89
1:0.7	2.13	95.64	3.60	96.01	4.67	98.29	5.83	90.97	91.29
1:01	2.10	90.68	1.78	95.46	1.09	84.11	6.73	93.76	84.11
1:02	1.90	96.69	0.94	93.87	1.21	73.52	1.45	80.89	73.52
1:05	1.07	77.72	1.36	59.59	0.58	59.41	1.17	56.25	59.41
1:10	0.93	13.95	1.00	11.33	0.10	13.04	0.71	12.25	13.04
1:15	0.72	50.16	0.37	1.37	1.57	3.88	0.93	1.90	3.88

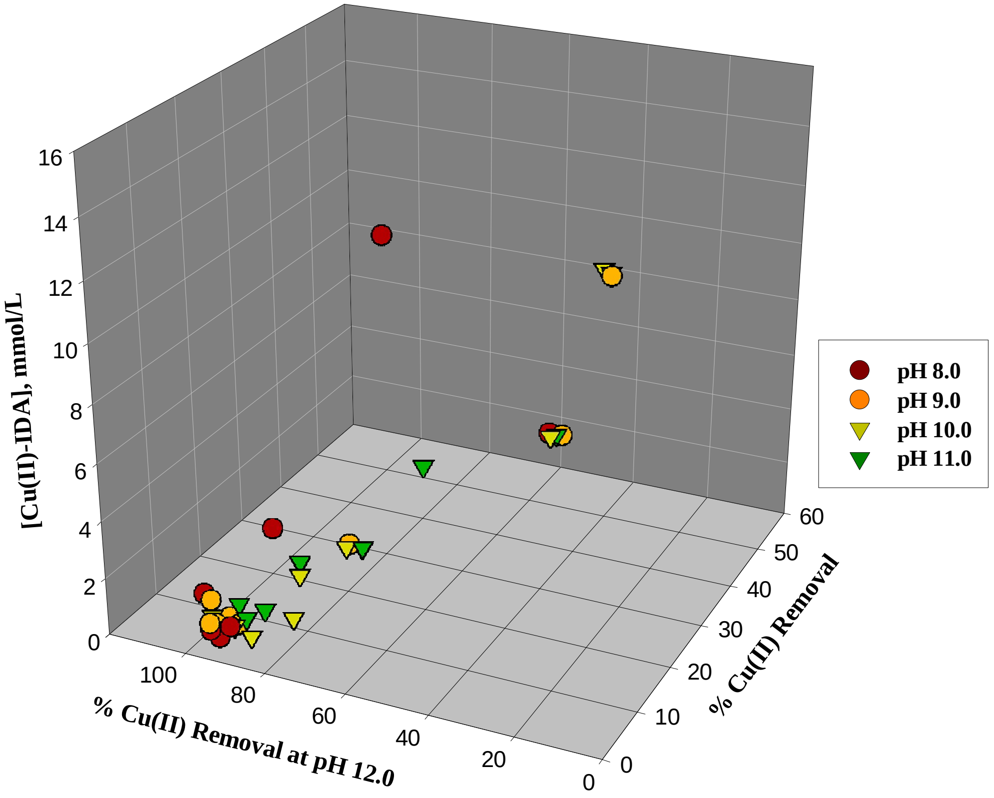


Figure 4.13. *Simultaneous removal of Cu(II) for different concentrations of Cu(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH values.*

4.2.2. Cu(II)-NTA System

4.2.2.1. Decomplexation and degradation of Cu(II)-NTA complex species

4.2.2.1.1. Effect of Cu(II)-NTA Concentration

The decomplexation and degradation of Cu(II)-NTA complexes was studied using a constant concentration of Fe(VI). Various doses of Cu(II)-NTA such as 0.5, 1.0, 5.0 and 15.0 mmol/L was treated with a constant dose of Fe(VI), 1.0 mmol/L at different pH values, i.e., pH 8.0, 9.0, 10.0 and 12,0. The UV-Vis data obtained was correlated for the removal of Fe(VI) for the studied molar ratios obtained at different pH values. The results obtained were shown in the figures 4.14 (a) to 4.14(c). These figures demonstrated that relatively fast decrease in the concentration of Fe(VI) occurred initially which slowed down gradually as the reaction time increases. Similar to Cu(II)-IDA, the increase in molar concentration of Cu(II)-NTA resulted in increase in degradation of Cu(II)-NTA with higher rate of decomposition of Fe(VI) occurred at different pH values.At pH 8.0, with the increase in concentration of Cu(II)-NTA from 0.5 to 15 mmol/L, the respective percent decrease in the concentration of Fe(VI) is from 10.99 to 43.49% within 30 mins of reaction time, the result suggesting that increasing the pollutant concentration, could effectively be treated with the regulated dose of Fe(VI). Results also indicated that at higher pH value, the removal of Cu(II)-NTA is retarded which is comprehensible with the higher reactivity of Fe(VI) at lower pH values. In fact, at higher pH 12.0, only insignificant change in the concentration of Fe(VI) in presence of Cu(II)-NTA was observed and hence data at pH 12.0 was not included herewith.

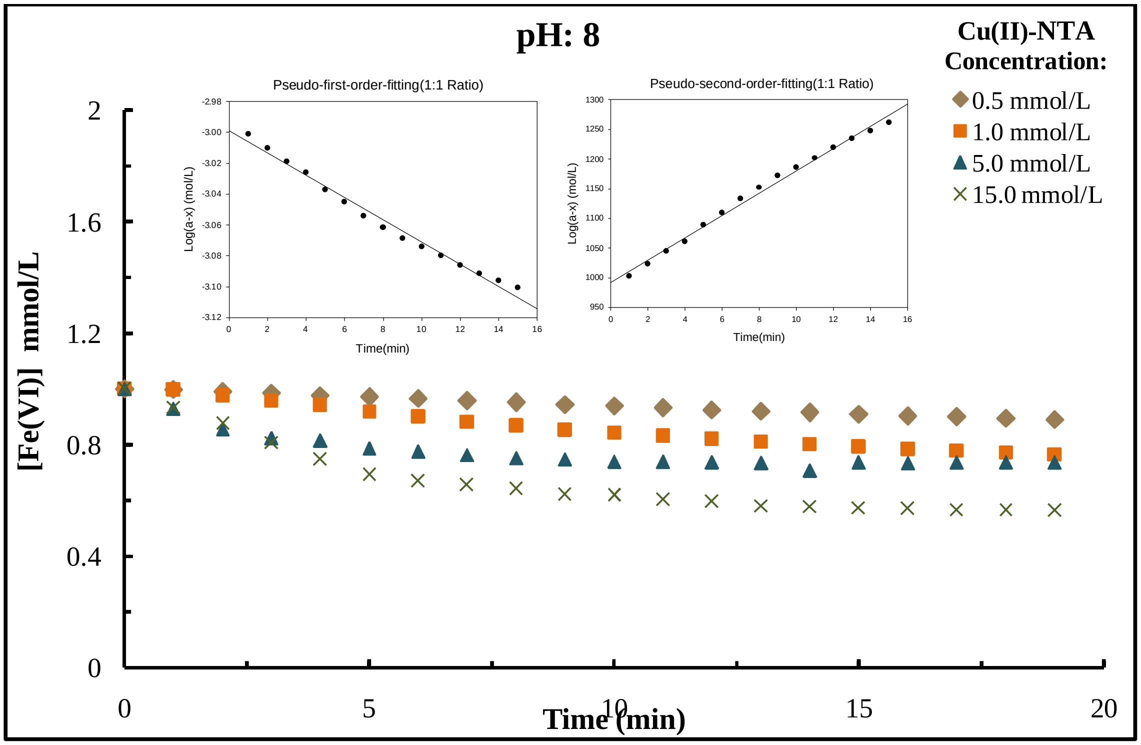


Figure 4.14(a). *Degradation of NTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-NTA at constant pH:8.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

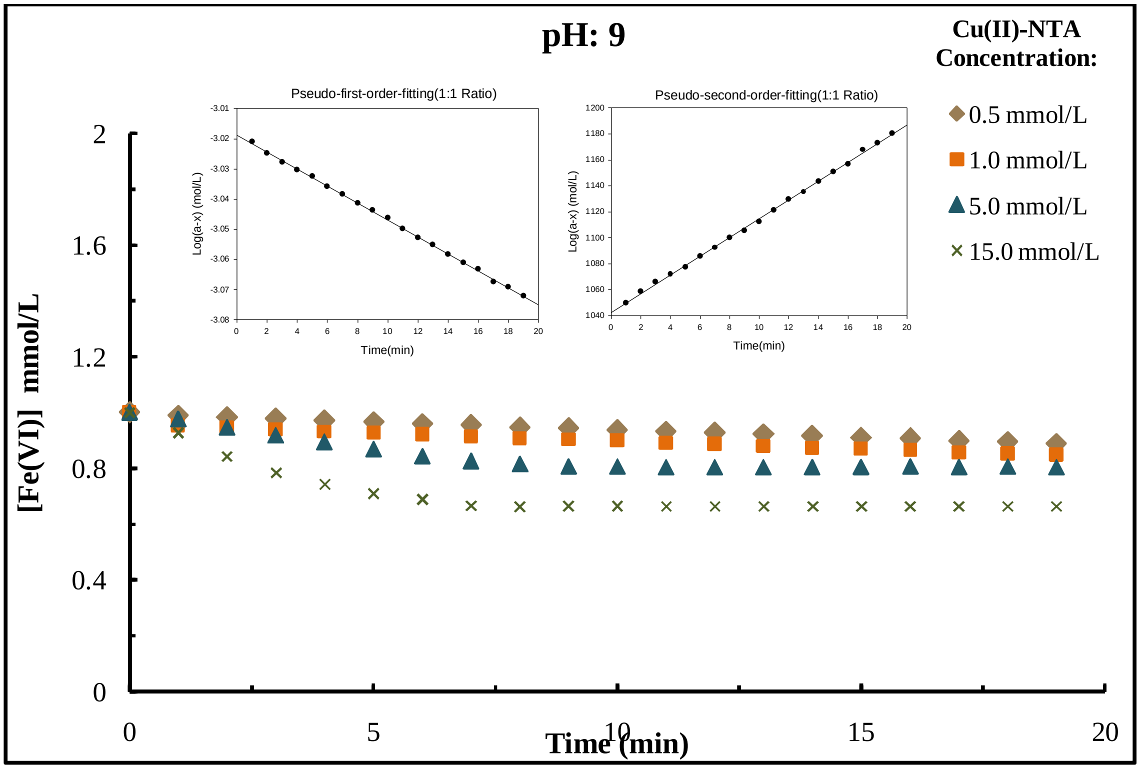


Figure 4.14(b). *Degradation of NTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-NTA at constant pH:9.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

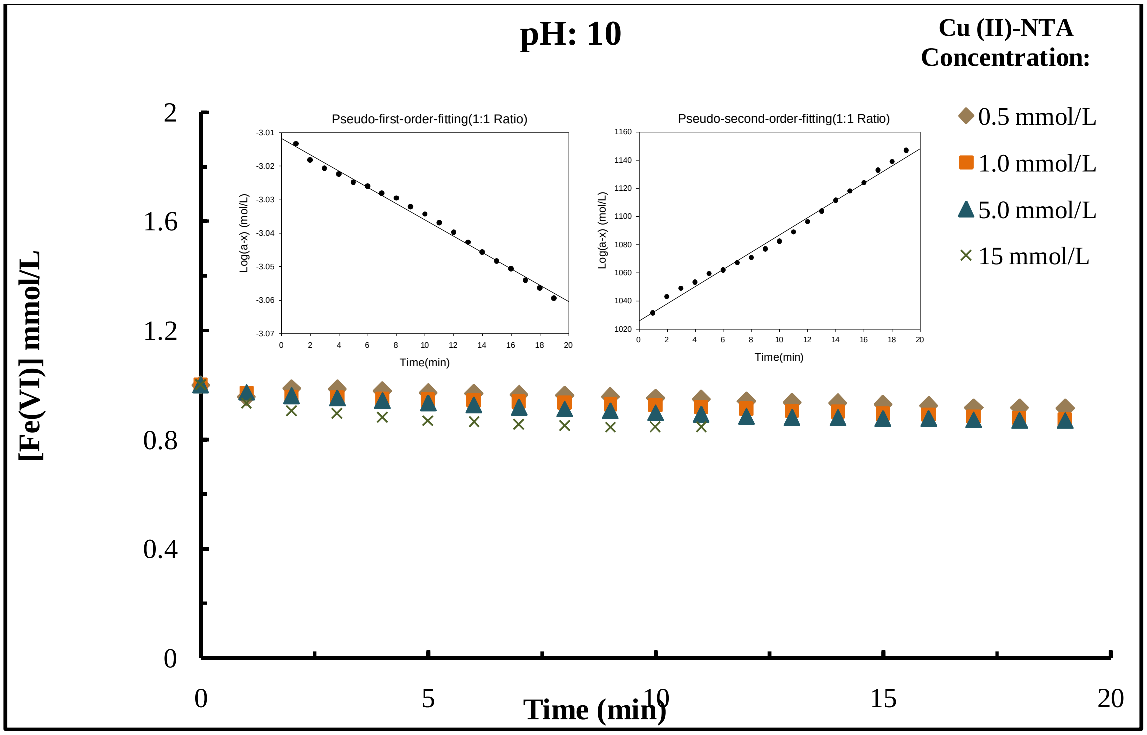


Figure 4.14(c). *Degradation of NTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-NTA at constant pH:10.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

4.2.2.1.2. Kinetics of Cu(II)-NTA decomplexation/degradation

Kinetics of the oxidation of Cu(II)-NTA in presence of Fe(VI) was carried out using the time dependence UV-Visible data collected at different pH values and molar ratios of Fe(VI) to Cu(II)-NTA. Assuming the same reductive pathways of Fe(VI) and rate laws for the reduction of Fe(VI), as already explained for the system of Cu(II)-IDA, the kinetics of the reduction of Fe(VI) was described with the Pseudo-first order and Pseudo-second order rate laws using the following equation (4.19):

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Cu(II)-NTA]^n \qquad \ldots (4.19)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)]^m \qquad \ldots (4.20)$$

$$\text{where, } k_1 = k\,[Cu(II)\text{-}NTA]^n \qquad \ldots (4.21)$$

The insets in figures4.14 (a) to 4.14(c) represent the fitting results of pseudo-first and pseudo-second order equations, respectively for pH 8.0, 9.0 and 10.0 having the 1:1 Fe(VI) and Cu(II)-NTA molar stoichiometry. The rate constants were obtained for both the pseudo-first and pseudo-second-order rate for all the varied molar ratios and at different pH values. The results were returned in Table 4.8. Results showed that the rate constant values 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 Cu(II)-NTA was increased at lower pH values. Quantitatively, decreasing the pH from 10.0 to 8.0, the rate constant was increased respectively from $0.4\text{x}10^{-2}$ to$1.61\ \text{x}10^{-2}$ min^{-1} (for pseudo-first-order) and from 6.10 to 17.10 L/mol/min (for pseudo-second-order) at the 1:1 molar ratios of Fe(VI) and Cu(II)-NTA.

Table 4.8. *Pseudo-first and Pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentration of Cu(II)-NTA at different pH conditions*

[Cu(II)-NTA] (mmol/L)	**Pseudo-first-order rate constant (x10^{-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	0.46	0.999	0.23	0.874	6.87	0.998	6.278	0.999	4.37	0.983
1.0	1.61	0.986	0.46	0.999	0.46	0.992	17.10	0.985	6.905	0.998	6.10	0.959
5.0	2.76	0.900	2.07	0.959	0.69	0.992	19.12	0.872	9.288	0.556	68.83	0.968
15.0	6.91	0.990	4.61	0.930	1.61	0.958	36.57	0.966	12.53	0.367	16.41	0.980

The overall rate constant 'k' was estimated using the rate constants, k_1 obtained for both pseudo-first-order as well as the pseudo-second-order rate law. The value of 'n' was estimated for 1 and 2 but it was best fitted for n=1; since the data was fairly fitted well to the pseudo-first-order rate constant values (*cf* Figure 4.15). The overall rate constant values along with the R^2 values, estimated using the pseudo-first-order rate constant values at different pH values are as shown in Table 4.9. In general, increasing the pH, 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 3.0 to 1.0 L/mol/min. The low pH values greatly favored the removal of Fe(VI) or in other words, possibly, an enhanced degradation of the organic pollutant took place at lower pH values.

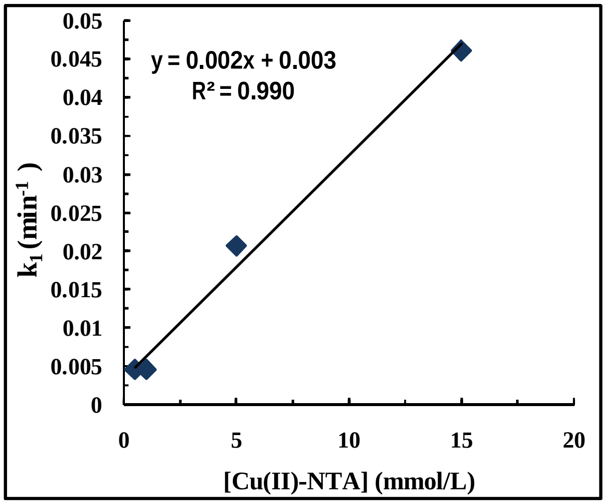


Figure 4.15. *Fitting of pseudo-first-order rate constant values for the degradation of Fe(VI) in presence of different concentrations of Cu(II)-NTA at pH 9.0*

Table 4.9. *Overall rate constant in the decomplexation/degradation of Cu(II)-NTA by ferrate(VI) at different pH conditions*

pH	Cu(II)-NTA System	
	k (L/mol/min)	**R^2**
8.0	3.0	0.811
9.0	2.0	0.929
10.0	1.0	0.842

4.2.2.2. Mineralization of NTA

The Fe(VI) treated samples of various stoichiometric ratios of Cu(II)-NTA and Fe(VI) at different pH values were further analyzed with the help of TOC analyzer. The total organic carbon data obtained for varied molar ratios (1:0.5 to 1:15) at p values, i.e. pH 8.0, 9.0, 10.0 and 12.0 are shown in table 4.10. The results were further presented graphically in figure 4.16.The degradation/mineralization of organic pollutant i.e., NTA took place significantly. It was also observed that the percent mineralization of NTA was relatively high at lower concentration of Cu(II)-NTA when treated with the same dose of Fe(VI). Decreasing the concentration of Cu(II)-NTA from 15.0 to 0.50 mmol/L, the corresponding increase in percent removal of TOC was found to be from 5.36% to 60.23%, respectively at pH 8.0; whereas similar increase, from 3.64% to 15.79 % was obtained at pH 12.0. These data again indicated that the pH values favored significantly the mineralization of NTA by Fe(VI).

Table 4.10. *Removal of NTA from Cu(II)-NTAcomplex species by Fe(VI) at different pH values*

pH	**% Mineralization of NTA in Cu(II)-NTA complex species by Ferrate(VI)**			
	Fe(VI) : [Cu(II)-NTA]			
	1:0.5	**1:01**	**1:05**	**1:15**
8	60.23	25.32	17.42	5.36
9	53.83	24.19	10.19	5.23
10	29.21	20.85	4.58	3.67
12	15.79	17.33	4.39	3.64

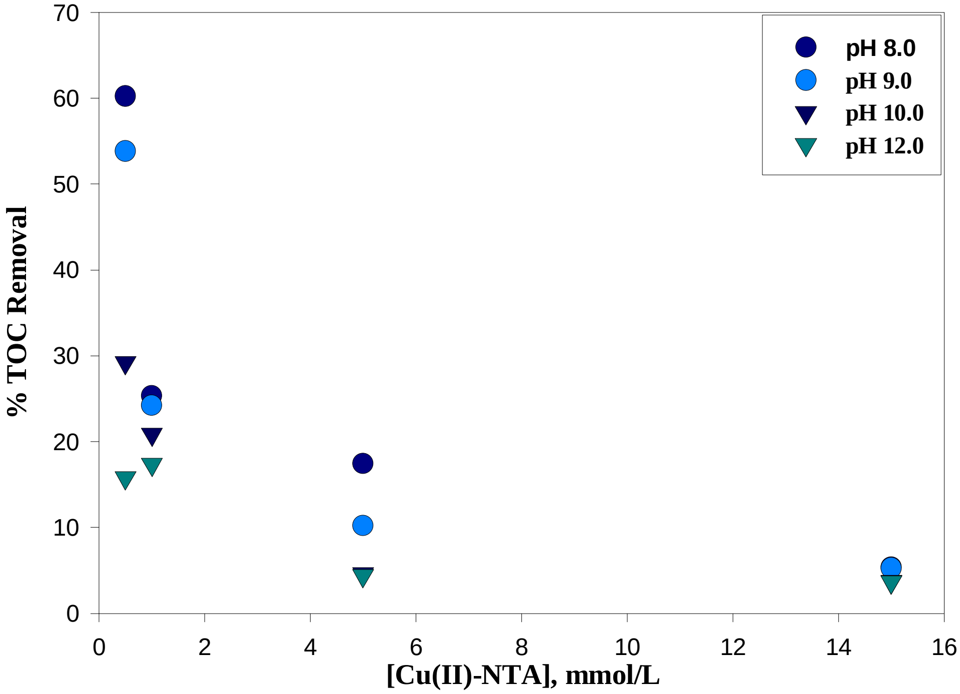


Figure 4.16. *Degradation of NTA for different concentrations of Cu(II)-NTA treated with Fe(VI):1.0 mmol/L at different pH values*

4.2.2.3. Simultaneous removal of Cu(II)

Simultaneous removal of Cu(II) from the Cu(II)-NTA contaminated water treated with Fe(VI) was further investigated with the help of AAS analysis at the treated pH as well as at higher pH values i.e., at pH 12.0 . The pH of treated solution was raised to pH 12.0 with the addition of drops of conc. NaOH. Results obtained by AAS analysis were presented in Table 4.11. Moreover, the results were also presented graphically as a function of molar concentration of Cu(II)-NTA in Figure 4.17.The data clearly indicated that a partial removal of Cu(II) occurred at lower pH values, however, very high percent removal of Cu(II) was observed when the solution pH was raised to pH 12; apparently due to an enhanced coagulation efficiency of Fe(VI) at higher pH values. Cu(II) was completely removed, i.e., percent removal of Cu(II) was 100% when the treated sample solution of Cu(II)-NTA (0.5 mmol/L) was raised to pH 12.0 whereas the percent removal of Cu(II) from the same sample solution was only 10.34 %, 25.00% and 30.80% respectively at pH 8.0, 9.0 and 10.0. Generally with the increase in molar concentration of Cu(II)-NTA, the percent removal of Cu(II) from the solution was decreased; obtained for each pH values. It was assumed that the reduction of Fe(VI) to Fe(III) helped in the removal of free Cu(II) ions from the solution through coagulation process when the initial concentration of Fe(VI) was kept constant. Therefore, increasing the concentration of Cu(II)-NTA caused for a decrease in percent removal of Cu(II) from the Fe(VI) treated samples. The coagulating capacity possessed with Fe(VI) was confirmed by the studies on the comparative turbidity removal performance of Fe(VI) as K_2FeO_4 with $FeSO_4.7H_20$ and $Fe(NO_3)_3$ which showed that the residual turbidity in treated water with Fe(VI) was less than that with Ferrous sulphate and ferric nitrate (Gray and Waite, 1983).

Table 4.11. *Percent Removal of Cu(II) by Fe(VI) for different molar ratio of Cu(II)-NTA and Fe(VI) at different pH values [Initial concentration of Fe(VI): 1.0 mmol/L]*

Fe(VI): Cu(II)-NTA	**% Removal of Copper(II) by Fe(VI)**						
	pH 8	**pH raised to 12**	**pH 9**	**pH raised to 12**	**pH 10**	**pH raised to 12**	**pH12**
1:0.5	10.34	100.00	25.00	100.00	30.80	100.00	100.00
1:01	3.33	75.00	12.00	84.00	15.50	47.37	92.31
1:10	10.10	20.21	3.61	31.05	5.90	5.68	28.63
1:15	2.77	10.79	0.71	12.46	1.20	3.41	12.2

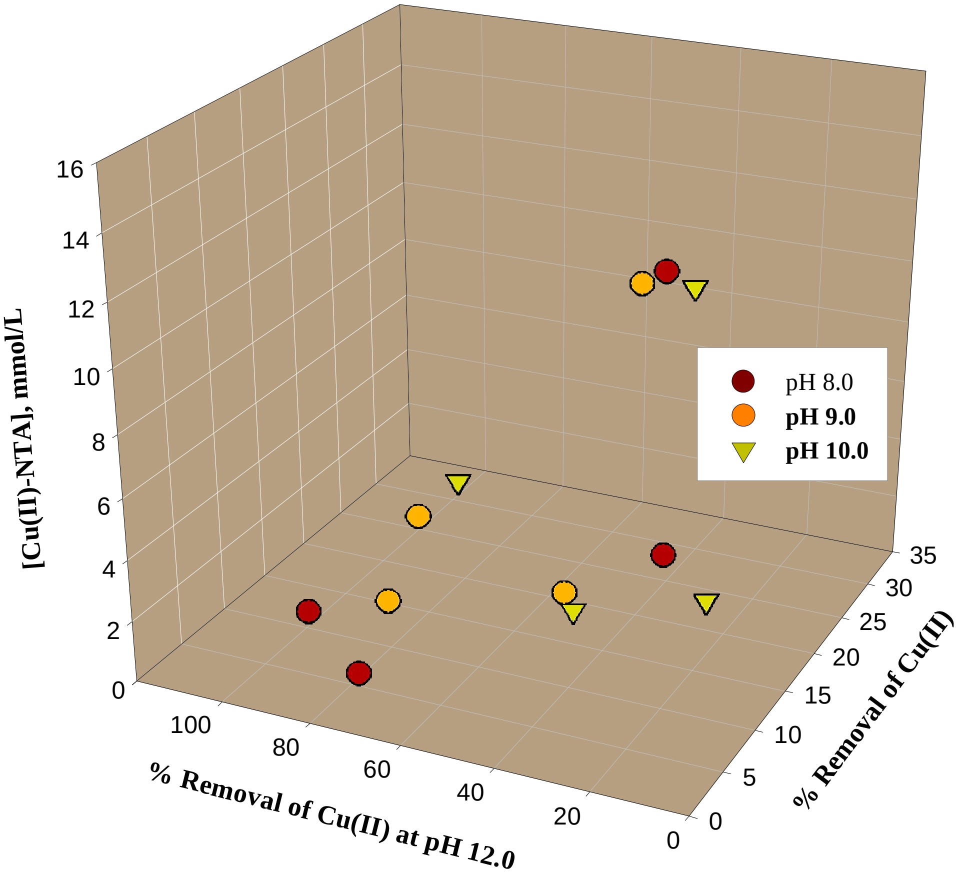


Figure 4.17. *Simultaneous removal of Cu(II) for different concentrations of Cu(II)-NTA treated with Fe(VI): 1.0 mmol/L at different pH values.*

4.2.3. Cu(II)-EDTA System

4.2.3.1. Decomplexation and degradation of Cu(II)-EDTA complex species

4.2.3.1.1. Effect of Cu(II)-EDTA Concentration

The change in Fe(VI) concentration obtained by the UV-Visible measurements in the treatment of Cu(II)-EDTA of 1.0 mmol/L was investigated for varied concentration of Cu(II)-EDTA, i.e., from 0.5 to 15.0 mmol/L with a constant dose of Fe(VI), 1.0 mmol/L and at different pH conditions i.e., pH 8.0, 9.0, 10.0 and 12.0. The UV-Visible data obtained were represented in figures 4.18(a) to 4.18(d). The results clearly indicated that reasonably a significant removal of Fe(VI) occurred in presence of Cu(II)-EDTA, especially at higher concentration of Cu(II)-EDTA. The increase in degradation of Fe(VI) with increasing concentration of Cu(II)-EDTA indicated that an enhanced value of Cu(II)-EDTA complex was degraded with an increased removal of Fe(VI) from solution. The rate of Fe(VI) removal was apparently higher at higher concentration Cu(II)-EDTA which was further increased at lower pH values. It was observed that almost a saturation stage of Fe(VI) removal occurred within 20 mins of contact and increasing the concentration of Cu(II)-EDTA from 0.3 to 15.0 mmol/L caused to increase the percent Fe(VI) removal from 10.95 to 43.49%. These results were again in line to the previous systems under study, explicable with the fact that the redox potential and hence the reactivity of Fe(VI) is higher at lower pH values.

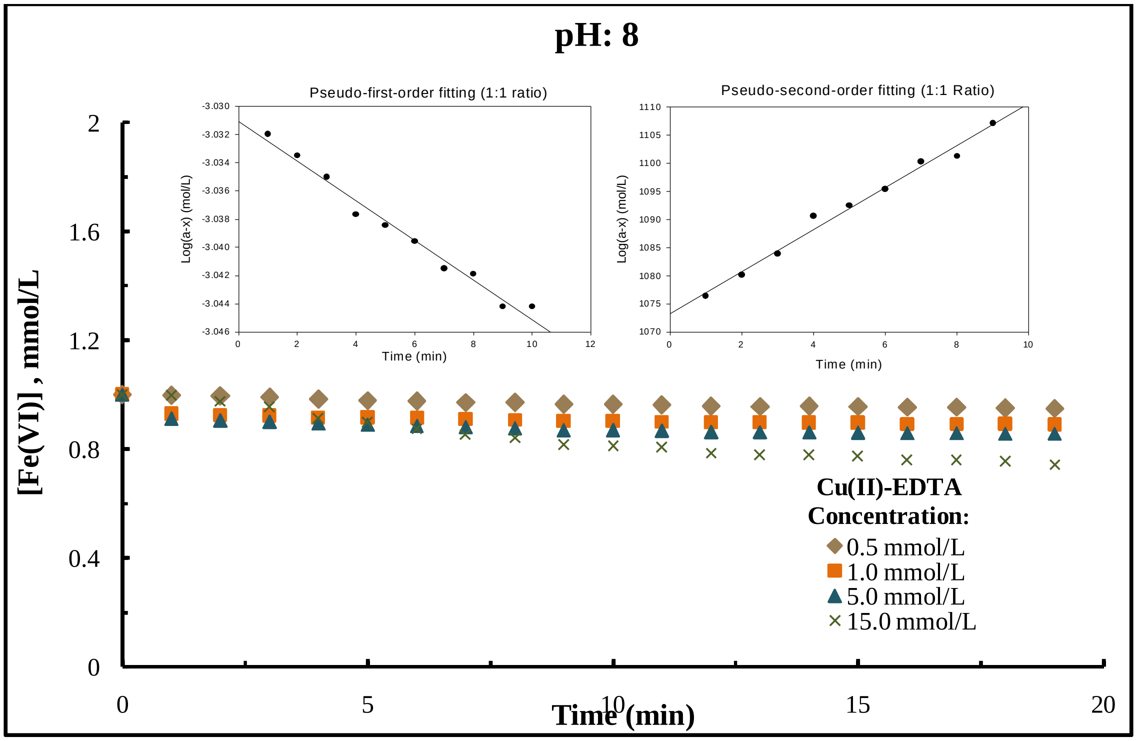


Figure 4.18(a). *Degradation of EDTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-EDTA at constant pH:8.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

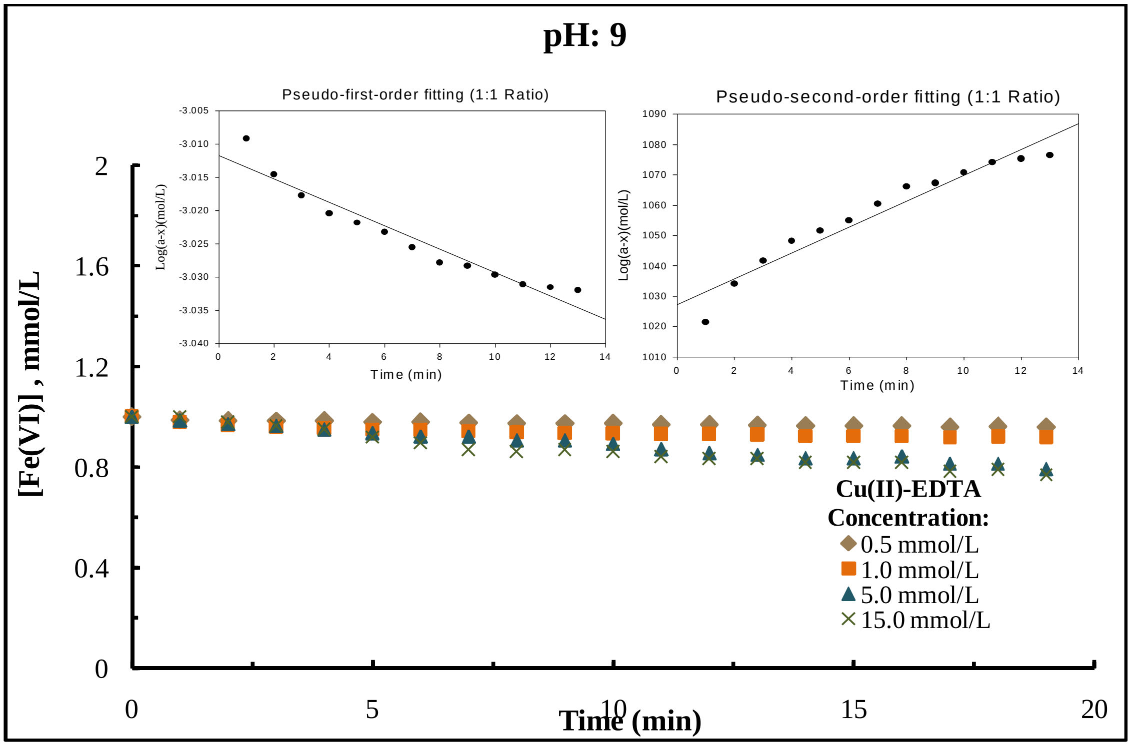


Figure 4.18(b). *Degradation of EDTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-EDTA at constant pH:9.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

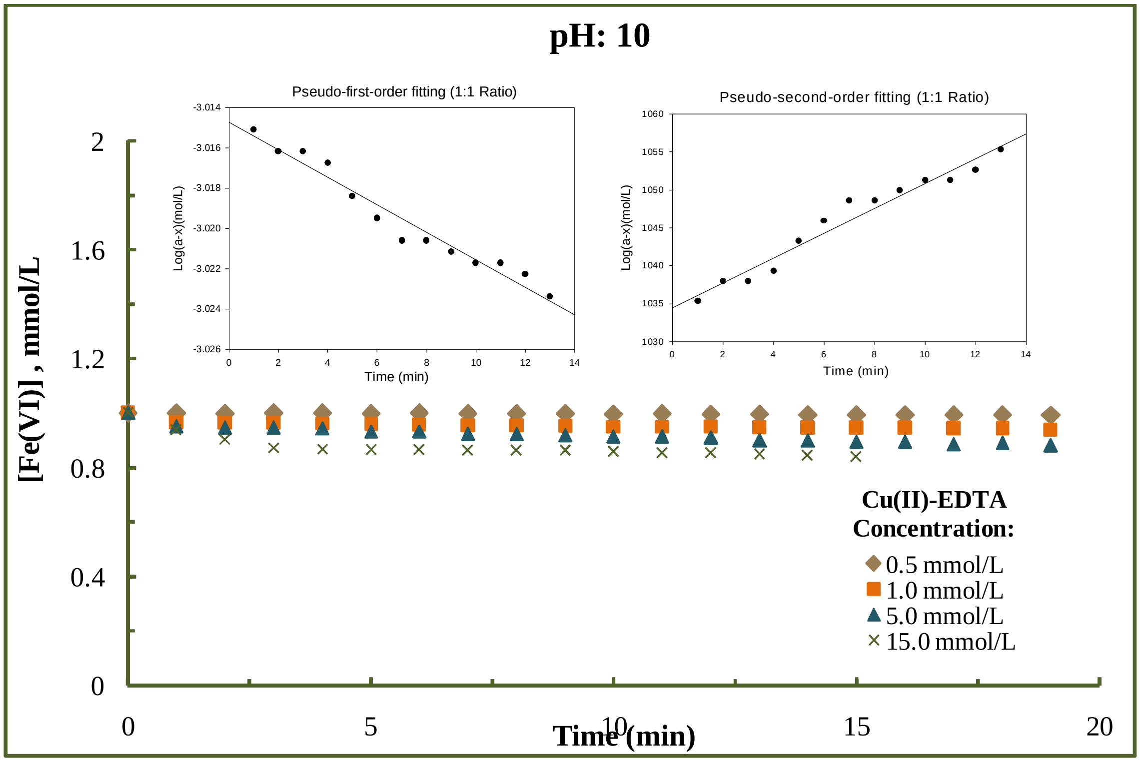


Figure 4.18(c). *Degradation of EDTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-EDTA at constant pH:10.0.[Initial [Fe(VI)]: 1.0 mmol/L]*

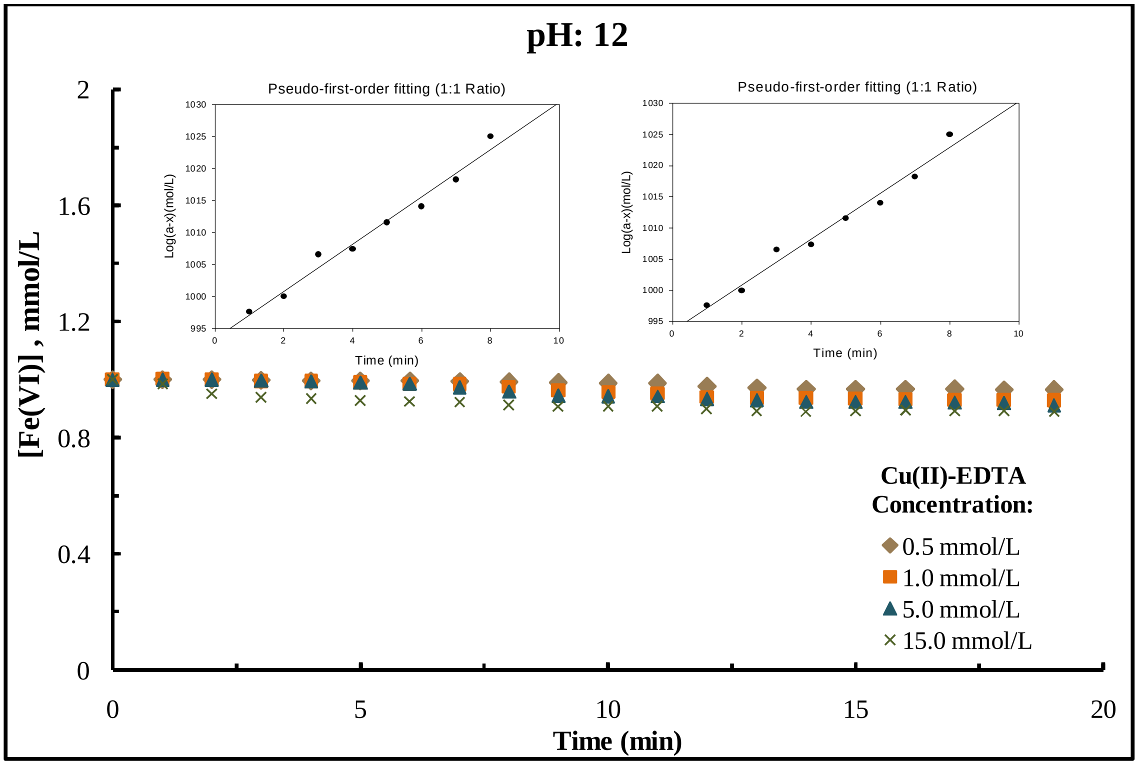


Figure 4.18(d). *Degradation of EDTA in presence of Fe(VI) as a function of time for different concentrations of Cu(II)-EDTA at constant pH:12.0.[Initial [Fe(VI)]: 1.0 mmol/L]*

4.2.3.1.2. Kinetics of Cu(II)-EDTA decomplexation/degradation

The kinetics of oxidation of Cu(II)-EDTA by Fe(VI) was studied at various molar ratios of Fe(VI) and Cu(II)-EDTA at different pH values. The rate law for removal of Fe(VI) in presence of Cu(II)-EDTA could be expressed as:

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Cu(II)-EDTA]^n \qquad \ldots (4.22)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)]^m \qquad \ldots (4.23)$$

$$\text{where} \quad k_1 = k\,[Cu(II)\text{-}EDTA]^n \qquad \ldots (4.24)$$

Estimating the rate constant by taking m=1 or 2 in equation (4.23);the pseudo-first and pseudo-second order rate kinetics were obtained and represented in the insets of the figures

4.18(a)-4.18(d), respectively for pH 8.0, 9.0, 10.0 and 12.0 having the 1:1 Fe(VI) and Cu(II)-EDTA molar stoichiometry. The rate constants obtained for both the pseudo-first and pseudo-second order rate for all the studied molar ratios and at different pH values were calculated and returned in Table 4.12. It was observed from the results that the rate constants was, in general, decreased with the increase in pH, however, apparently the decrease was less pronounced at lower concentrations of Cu(II)-EDTA, compared to the higher concentrations of Cu(II)-EDTA. Quantitatively, decreasing the pH from 12.0 to 8.0 the rate constant was increased, respectively from $1.11\text{x}10^{-2}$ to $3.45\text{x}10^{-2}$ min^{-1} (for pseudo-first-order) and from 7.018 to 27.80 L/mol/min (for pseudo-second-order), obtained at 15.0 mmol/L concentration of Cu(II)-EDTA. Apparently, Cu(II)-EDTA was relatively stable toward its decomposition by Fe(VI), compared to the other species viz., Cu(II)-IDA, Cu(II)-NTA etc. The stability of the Cu(II)-EDTA is ascribed due to its higher stability constant values than the Cu(II)-IDA and Cu(II)-NTA stability constants (Table 4.32).

Table 4.12. *Pseudo-first and Pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentration of Cu(II)-EDTA at different pH conditions.*

[Cu(II)-EDTA (mmol/L)	**Pseudo-first-order rate constant (x10^{-2}) (1/min)**								**Pseudo-second-order rate constant (L/mol/min)**							
	pH 8.0		**pH 9.0**		**pH 10.0**		**pH 12.0**		**PH 8.0**		**pH 9.0**		**pH 10.0**		**pH 12.0**	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.5	0.23	0.93	0	0.99	0	0.889	0	0.957	2.768	0.933	1.762	0.977	4.086	0.889	2.476	0.93
1.0	0.23	0.981	0.23	0.933	0.00	0.952	0.23	0.977	3.73	0.986	4.26	0.984	1.618	0.981	3.686	0.976
5.0	0.46	0.982	0.92	0.978	0.23	0.952	0.46	0.943	4.1	0.935	14.06	0.984	4.69	0.986	6.004	0.945
15.0	3.45	0.984	1.60	0.984	1.84	0.904	1.15	0.849	27.80	0.988	15.32	0.960	6.119	0.902	7.018	0.866

Using both the values of k_1 in equation (4.24), the overall rate constant 'k' was estimated by taking n=1 or 2. It was further observed that the best fitting was obtained with the k_1 values obtained by the pseudo-first order rate constants along with the n=1. These results indicated that 1:1 stoichiometry occurred with the Fe(VI) and Cu(II)-EDTA since the kinetic data was best fitted with m=1 and n-1. Figure 4.19 represented the fitting of the pseudo-first-order rate constant values at pH 9.0. The overall rate constant values along with the R^2 were estimated accordingly at different pH values and the results were returned in Table 4.13. Table clearly indicated that with the increase in pH, the overall rate constant was generally decreased.

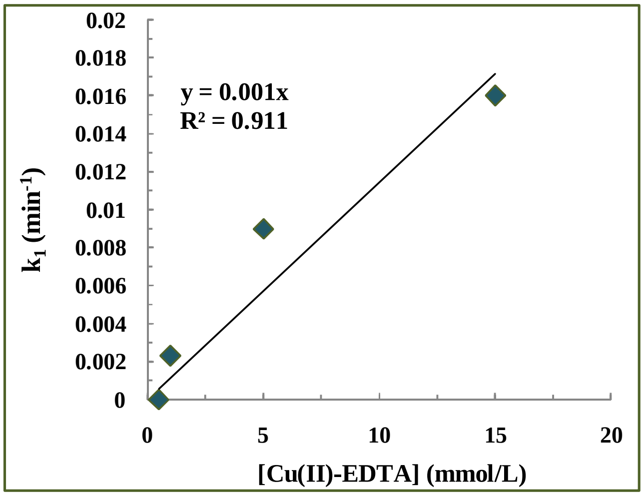


Figure 4.19. *Fitting of pseudo-first-order rate constant values for the degradation of Fe(VI) in presence of different concentrations of Cu(II)-EDTA at pH 9.0.*

Table 4.13:. *Overall rate constant in the decomplexation/degradation of Cu(II)-EDTA by ferrate(VI) at different pH conditions*

pH	Cu(II)-EDTA System	
	k (L/mol/min)	R^2
8	2.0	0.940
9	1.0	0.911
10	1.0	0.937

4.2.3.2. Mineralization of EDTA

It was assumed that the Fe(VI) caused in decomplexation of Cu(II)-EDTA followed by the degradation or mineralization of EDTA. Therefore, the Fe(VI) treated Cu(II)-EDTA samples were subjected toward the TOC analysis. The percent removal of TOC obtained for various concentrations of Cu(II)-EDTA at different pH values, i.e., 8.0, 9.0, 10 and 12.0 were obtained and returned in Table 4.14; also represented in Figure 4.20. The results indicated that at lower pH values relatively higher percent of the EDTA was mineralized. Moreover, increase in concentration of Cu(II)-EDTA resulted in lower percent degradation of EDTA. Increasing the concentration of Cu(II)-EDTA from 0.5 to 15.0 mmol/L, the decrease in percent removal of TOC was found to be from 70.0% to 31.37% at pH 8.0 indicating that more percent of EDTA was degraded at lower concentration of Cu(II)-EDTA as treated with constant dose of Fe(VI). Decomplexation of Cu(II)-EDTA occurred, more at lower pH; obviously resulted in higher percent removal of EDTA. Therefore, the acidic conditions favored greatly the decomplexation and mineralization of EDTA (Tiwari *et al.*, 2008).

Table 4.14. *Removal of EDTA from Cu(II)-EDTA complex species by Fe(VI) at different pH values*

pH	**% Removal of EDTA using Ferrate(VI)**			
	Fe(VI) : [Cu(II)-EDTA]			
	1:03	**1:01**	**1:05**	**1:15**
8	70.00	64.55	53.35	31.37
9	57.23	55.30	41.80	26.40
10	50.00	54.20	40.70	21.44
12	6.42	32.11	28.63	14.21

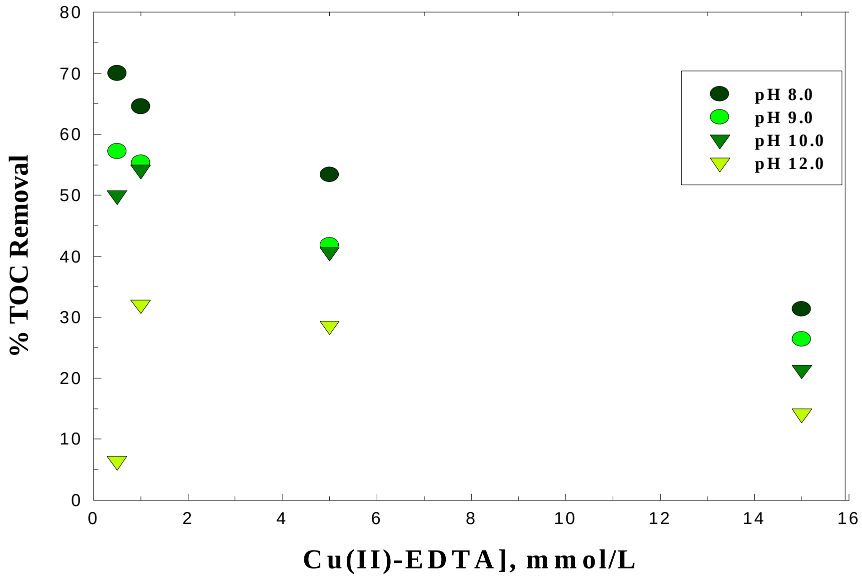


Figure 4.20. *Degradation of EDTA for different concentrations of Cu(II)-EDTA treated with Fe(VI):1.0 mmol/L at different pH values*

4.2.3.3. Simultaneous removal of Cu(II)

The simultaneous removal of Cu(II) from the Cu(II)-EDTA samples was further investigated by subjecting the Fe(VI) treated and filtered samples for AAS analysis. Additionally, the pH of the each treated sample solution was raised to 12.0 by adding drops of conc. NaOH and again filtered using 0.45µm syringe filter and then subjected for total Cu(II) concentration using AAS. The percent removal of Cu(II) from the obtained AAS data for the various concentrations of Cu(II)-EDTA and at different pH and the corresponding value raised at pH 12.0 were shown in Table 4.15; also represented with 3D graph in Figure 4.21.Results indicated that relatively low percent removal of Cu(II) occurred at lower pH values, however, with the increase in pH, significant increase in percent removal of Cu(II) was observed. Moreover, the removal of Cu(II) was observed higher at lower concentration of Cu(II)-EDTA, which was in accordance to the kinetic data studied previously. Almost 100% of Cu(II) was removed at the Cu(II)-EDTA concentration of 0.5 mmol/L treated at different pH values but coagulated at pH 12.0. These results again indicated that a significant amount of Cu(II) was removed simultaneously by the Fe(VI) treatment. It inferred a multipurpose utility of Fe(VI) in the treatment of wastewaters contaminated with Cu(II)-EDTA species.

Table 4.15. *Percent Removal of Cu(II) by Fe(VI) for different molar ratio of Cu(II)-EDTA and Fe(VI) at different pH values [Initial concentration of Fe(VI): 1.0 mmol/L]*

Fe(VI): Cu(II)-EDTA	**% Removal of Copper by Fe(VI)**						
	pH 8	**Raised to pH 12**	**pH 9**	**Raised to pH 12**	**pH 10**	**Raised to pH 12**	**pH12**
1:05	2.00	100.00	11.11	100.00	50.00	100.00	100.00
1:01	1.35	35.14	2.56	41.03	2.63	47.37	26.67
1:10	0.38	13.96	1.49	7.43	0.38	5.68	4.21
1:15	0.42	5.67	1.56	4.84	0.14	3.41	2.13

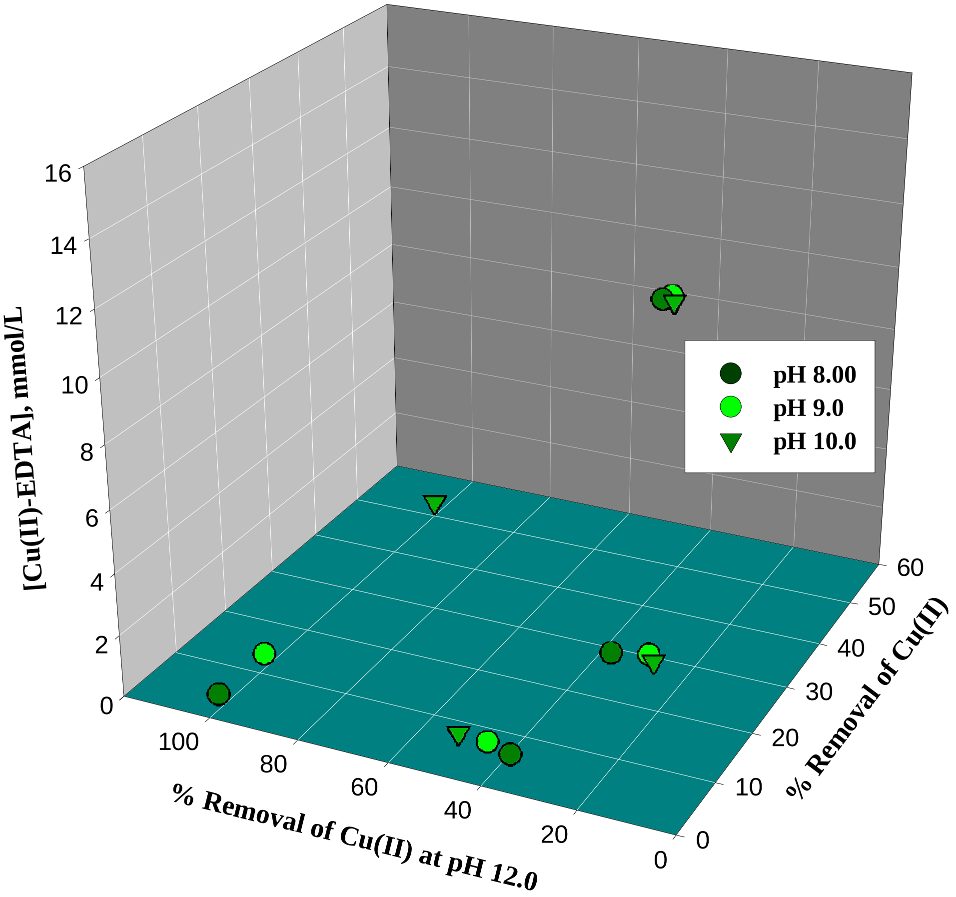


Figure 4.21. *Simultaneous removal of Cu(II) for different concentrations of Cu(II)-EDTA treated with Fe(VI): 1.0 mmol/L at different pH values.*

4.2.4. Cd(II)-IDA system

4.2.4.1. Decomplexation and degradation of Cd(II)-IDA complex species

4.2.4.1.1. Effect of Cd(II)-IDA Concentration

The UV-Visible analysis was performed to study the degradation of Cd(II)-IDA complexes treated with Fe(VI). The change in Fe(VI) removal was obtained and hence the data was correlated to the Cd(II)-IDA degradation. Different molar concentrations of Cd(II)-IDA, i.e., from 0.3 to 15.0 mmol/L was treated with a constant does of Fe(VI), i.e., 1.0 mmol/L at different pH values ranging from pH 8.0 to 10.0. The change in concentration of Fe (VI) which was due to the degradation of Cd(II)-IDA complex was observed by recording the change in the absorbance of the Fe(VI) treated solution at 510 nm as a function of time. The necessary correction for self-degradation of Fe(VI) at the studied pH was performed while obtaining the change in Fe(VI) concentration. Therefore, the change in Fe(VI) concentration as a function of time for different Cd(II)-IDA concentrations were obtained for the pH values 8.0, 9.0 and 10.0. The results obtained were presented in Figures 4.22(a), 4.22(b) and 4.22(c), respectively for pH 8.0, 9.0 and 10.0. Similar to other systems studied, percent decomposition of Fe(VI) occurred higher at elevated concentration of Cd(II)-IDA which indicated that more and more degradation of IDA was likely to occur at higher concentration of Cd(II)-IDA. It was further observed that a fast initial removal of Fe(VI) was observed and was slowed down in the latter stage of Fe(VI) treatment. For Example, taking Fe(VI) and Cd(II)-IDA concentrations as1.0 mmol/L and 10.0 mmol/L, respectively studied at pH 8; just within 7 mins of contact time almost an apparent equilibrium was attained and hence, a maximum removal of Fe(VI) was obtained and no further decrease in Fe(VI) concentration was recorded. This initial fast rate of decrease in Fe(VI) was, however, slowed down as pH was increased further, reaffirming that Fe(VI) was more stable or less reactive at higher pH values, explicable with the redox potential of Fe(VI) [2.20 and 0.72 at pH 1 and pH 14 respectively]. Similar observations were reported for other metal organo complexed systems elsewhere (Yang *et al.*, 2007, 2010).

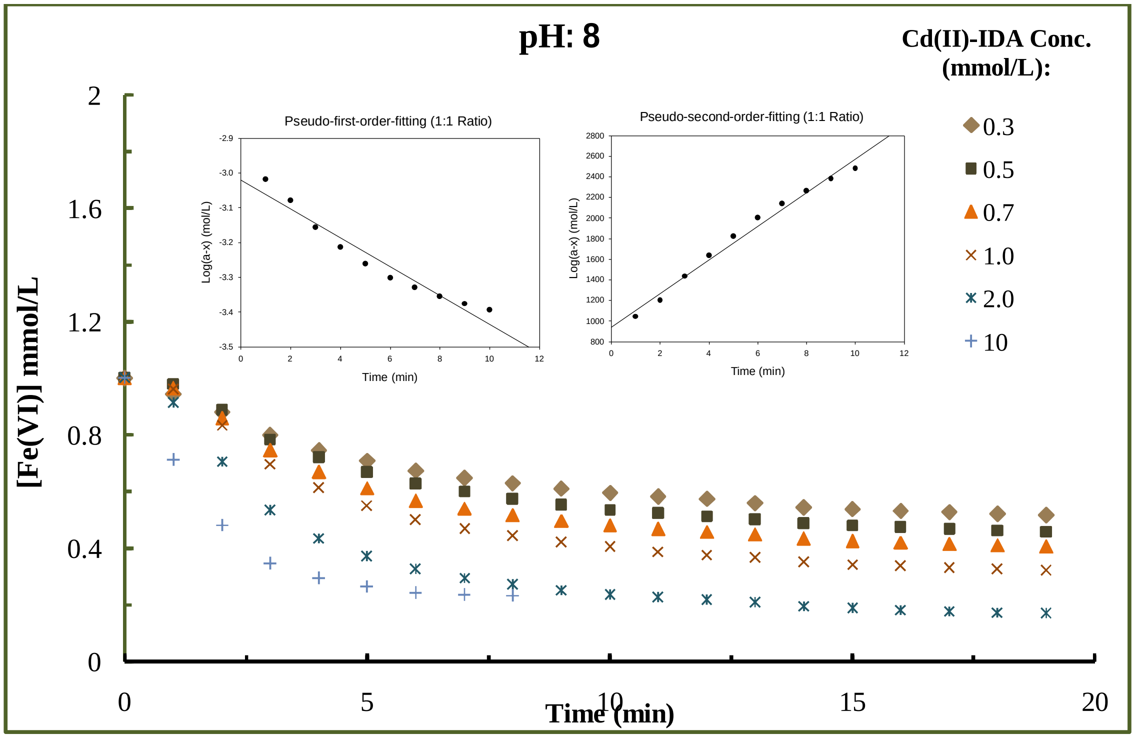


Figure 4.22(a). *Degradation of IDA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-IDA at constant pH:8.0 [Initial conc. of Fe(VI):1.0 mmol/L]*

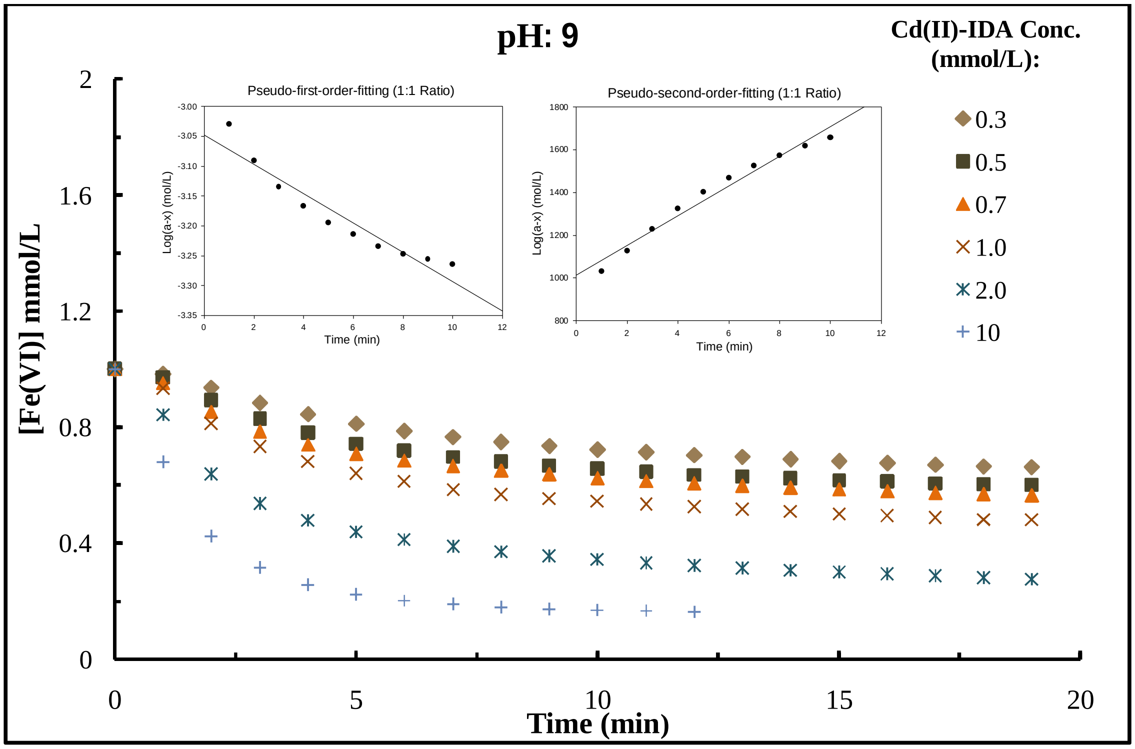


Figure 4.22(b). *Degradation of IDA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-IDA at constant pH:9.0 [Initial conc. of Fe(VI):1.0 mmol/L]*

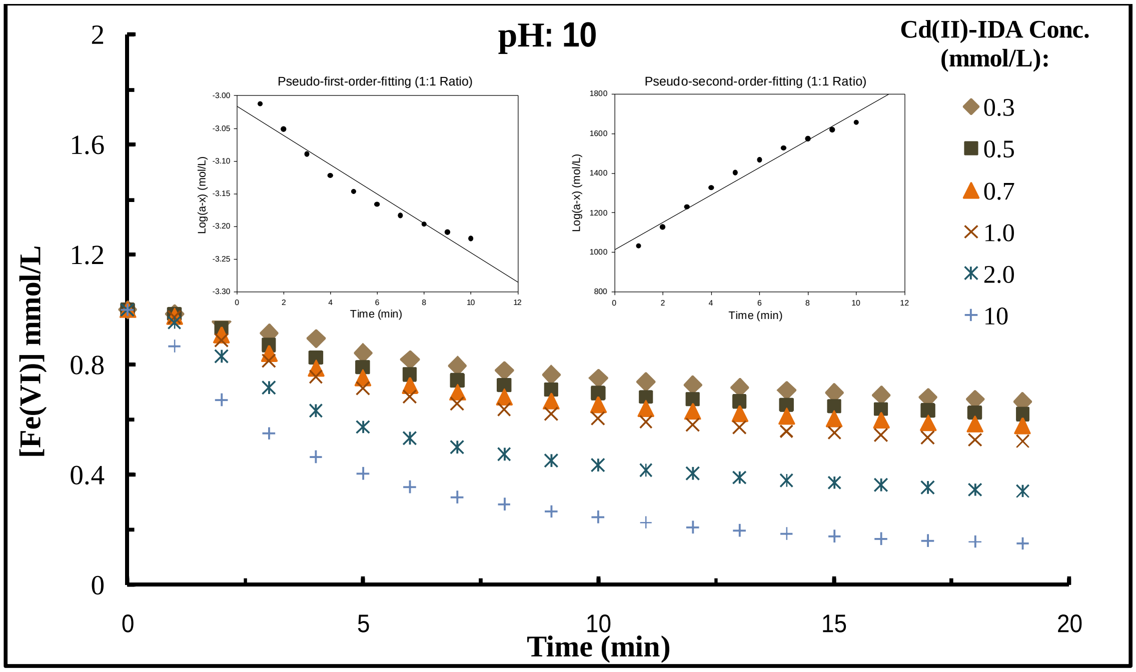


Figure 4.22(c). *Degradation of IDA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-IDA at constant pH:10.0 [Initial conc. of Fe(VI):1.0 mmol/L]*

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

The kinetics of the removal of Fe(VI) in presence of various concentrations of Cd(II)-IDA was carried out using the time dependence UV-Visible data collected at different pH values and molar ratios of Fe(VI) to Cd(II)-IDA. Assuming the same reductive pathways of Fe(VI) and rate laws for the reduction of Fe(VI) in presence of metal organic complexes as described for the previous systems, the kinetics of the reduction of Fe(VI) was described with pseudo-first order and pseudo-second order rate laws employing the following equations:

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Cd(II)-IDA]^n \qquad \ldots (4.25)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1 \times [Fe(VI)]^m \qquad \ldots (4.26)$$

$$\text{where } k_1 = k[Cd(II)-IDA]^n \qquad \ldots (4.27)$$

The fitting results of pseudo-first and pseudo-second order equations are represented in figures4.22(a), 4.22(b) and 4.22(c) respectively for pH 8.0, 9.0 and 10.0 having the 1:1 Fe(VI) and Cd(II)-IDA molar stoichiometry. The rate constants obtained for both the pseudo-first and second-order rate constants for all the varied molar ratios and at different pH values were obtained and hence returned in Table 4.16. Results showed that the rate constant was 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)-IDA was more pronounced at lower pH values. Quantitatively, decreasing the pH from 10.0 to 8.0, the rate constant was increased, respectively from $5.99x10^{-2}$ to $14.28x10^{-2}min^{-1}$ (for pseudo-first-order) and from 45.93 to 113.2 L/mol/min (for pseudo-second-order) at the 1:1 molar ratios of Fe(VI) and Cd(II)-IDA.

Table 4.16. *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 (x10^{-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

The overall rate constant ‘k’ was again estimated using the rate constants, k_1 obtained for both pseudo-first-order as well as the pseudo-second-order rate law. The value of ‘n’ was again estimated for 1 and 2; it was best fitted for n=1; since the data was fairly fitted well to the pseudo-first-order rate constant values (*cf* Figure 4.23). The overall rate constant values along with the R^2 values, estimated using the pseudo-first-order rate constant values at different pH values are as shown in Table 4.17. In general, increasing the pH, 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. This was again in accordance to the reactivity of the ferrate(VI) in solution since the protonated ferrate species ($HFeO_4^- \leftrightarrow H^+ + FeO_4^{2}$; pK_a^2=7.3) possessed with larger spin density than the deprotonated species (Ohta *et al.*, 2001; Sharma *et al.*,2004).1:1 stoichiometry for Cd(II)-IDA:Fe(VI) was also clearly demonstrated in the decomplexation/degradation of Cd(II)-IDA with ferrate(VI).

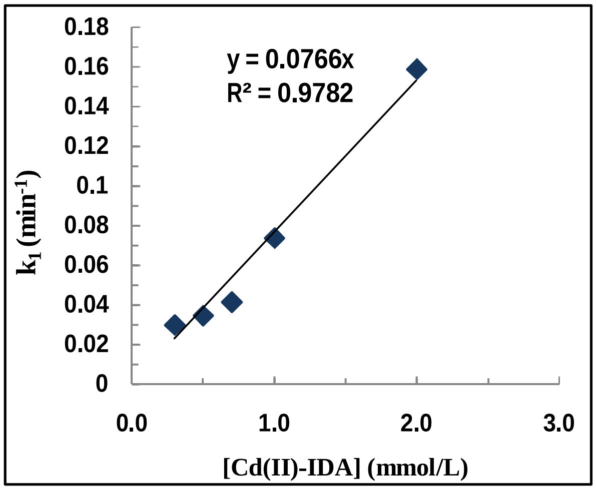


Figure 4.23. *Fitting of pseudo-first-order rate constant values for the degradation of Fe(VI) in presence of different concentrations of Cd(II)-IDA at pH 9.0.*

Table 4.17. *Overall rate constant in the decomplexation/degradation of Cd(II)-IDA by ferrate(VI) at different pH conditions*

pH	**Cd(II)-IDA System**	
	k(L/mol/min)	**R^2**
8.0	126.7	0.9775
9.0	76.6	0.9782
10.0	51.7	0.9641

4.2.4.2. Mineralization of IDA

The total organic carbon data was obtained from the Fe(VI) treated samples of Cd(II)-IDA. The results were collected for different concentrations of Cd(II)-IDA at different pH conditions (8.0, 9.0 and 10.0) treated with constant Fe(VI) doses and results were shown in Table 4.18 and also presented graphically in the 3D graph Figure 4.24. It was observed that organic IDA species was effectively degraded/mineralized by Fe(VI). The IDA was mineralized completely even up to the concentration of Cd(II)-IDA, 1.0 mmol/L. However, at higher concentration of Cd(II)-IDA, i.e., 2.0 to 10.0 mmol/L, the degradation of IDA was lowered significantly at all studied pH conditions. Lower pH values favored significantly the degradation of organic component in solution. Increasing the pH from 8.0 to 12.0, the corresponding decrease in TOC percent removal was found to be decreased from 41.80% to 22.60%, respectively for the constant dose of Fe(VI) and at Cd(II)-IDA concentration of 10.0 mmol/L. It was reported previously that cetylpyridinium chloride (CPC) was mineralized upto 95% by Fe(VI) with the results indicating that the aliphatic chain of CPC was mineralized to inorganic carbon in the initial reaction of Fe(VI) with CPC (Eng *et al.*, 2005)

Table 4.18. *Removal of IDA from Cd(II)-IDA complex species by Fe(VI) at different pH values*

pH	**% Mineralization of IDA using Ferrate(VI)**					
	Fe(VI) : [Cd(II)-IDA]					
	1:0.3	**1:0.5**	**1:0.7**	**1:1**	**1:2**	**1:10**
8	100.00	100.00	100.00	100.00	85.30	41.80
9	100.00	100.00	100.00	100.00	70.80	30.40
10	100.00	100.00	100.00	100.00	57.50	22.60

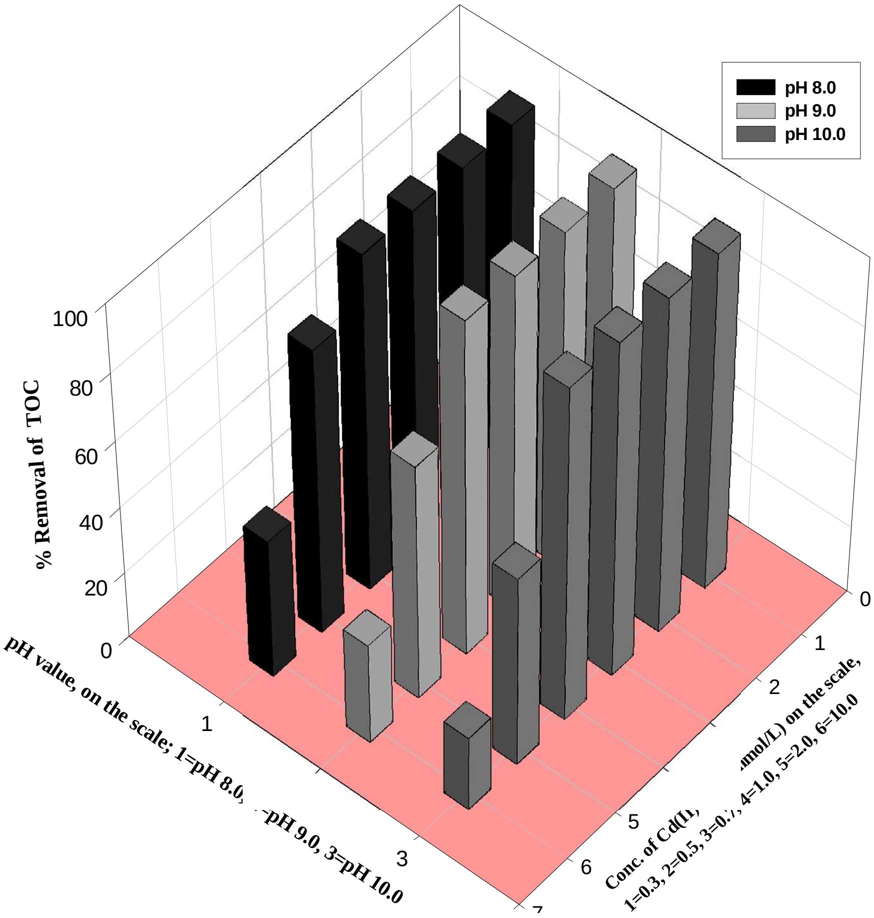


Figure 4.24. *Degradation of IDA for different concentrations of Cd(II)-IDA treated with Fe(VI)of 1.0 mmol/Lat different pH values.*

4.2.4.3. Simultaneous removal of Cd(II)

The simultaneous removal of Cd(II) from the Cd(II)-IDA treated samples through coagulation/adsoption by Fe(VI) was again investigated by ASS analysis. The treated sample solution were also raised to pH 12.0 using drops of NaOH , filtered and again subjected to AAS analysis. With the AAS data obtained, percent removal of Cd(II) was calculated for each molar ratio of Fe(VI) and Cd(II)-IDA at different pH and the same was calculated for the corresponding pH 12.0 . The results were tabulated in table 4.19 and also represented in 3D graph in Figure 4.25. Once again, the results showed that increasing pH results in sharp increase in higher percent removal of Cd(II), apparently due to enhanced coagulation capacity of Fe(VI) at higher pH. Complete removal of Cd(II), i.e, 100 % removal by Fe(VI) treatment was observed for most of the concentrations of Cd(II)-IDA except for the higher 10mmol/L, when the pH was raised from 8.0, 9.0 and 10.0 respectively to 12.0. Other studies also reported complete removal of free copper in case of Cu(II) cynide complex and also partial removal of Ni(II) from Ni(II) cyanide complexes (Lee and Tiwari, 2009).

Table 4.19. *Percent Removal of Cd(II) by Fe(VI) for different molar ratio of Cd(II)-IDA and Fe(VI) at different pH values [Initial concentration of Fe(VI): 1.0 mmol/L]*

Fe(VI): Cd(II)-IDA	**% Removal of Cadmium by Fe(VI)**					
	pH 8	**Raised to pH 12**	**pH 9**	**Raised to pH 12**	**pH 10**	**Raised to pH 12**
1:0.3	54.12	100.00	17.14	100.00	16.25	100.00
1:0.5	50.00	100.00	27.45	100.00	16.00	100.00
1:0.7	45.67	100.00	14.86	100.00	12.33	100.00
1:1	44.94	100.00	14.43	100.00	10.53	97.89
1:2	31.45	100.00	12.66	100.00	3.14	98.74
1:10	2.30	67.76	0.66	55.30	0.66	61.39

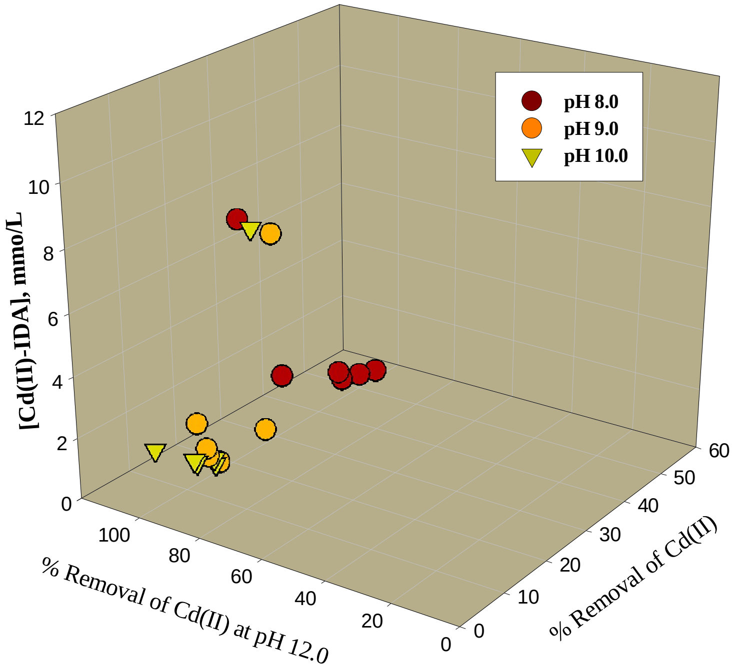


Figure 4.25. *Simultaneous removal of Cd(II) for different concentrations of Cd(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH values.*

4.2.5. Cd(II)-NTA system

4.2.5.1. Decomplexation and degradation of Cd(II)-NTA complex species

4.2.5.1.1. Effect of pH

Effect of pH on the treatment of Cd(II)-NTA complex by Fe(VI) was carried out by treating Cd(II)-NTA solution with molar concentration of 5.0 x10^{-4} mol/L with 1.0x10^{-4} Fe(VI) dose at different pH values ranging from 8.0 to 12.0. The UV-Visible data recorded for observing the change in concentration of Fe(VI) and it was further converted in to percent ferrate reduction as a function of time at different pH conditions. Results were presented graphically in Figure 4.26 which clearly demonstrated that a rapid Fe(VI) reduction was observed at pH 8.0 in initial reaction time but much less Fe(VI) reduction was noticed at higher solution pH. This fast increase in Fe(VI) percent decomposition intended that the reactivity of Fe(VI) increases decreasing the pH as at pH 1.0, the redox potential of Fe(VI) was 2.20 V whereas it was reported to be 0.72 V at pH 14.0. (Wood, 1985)

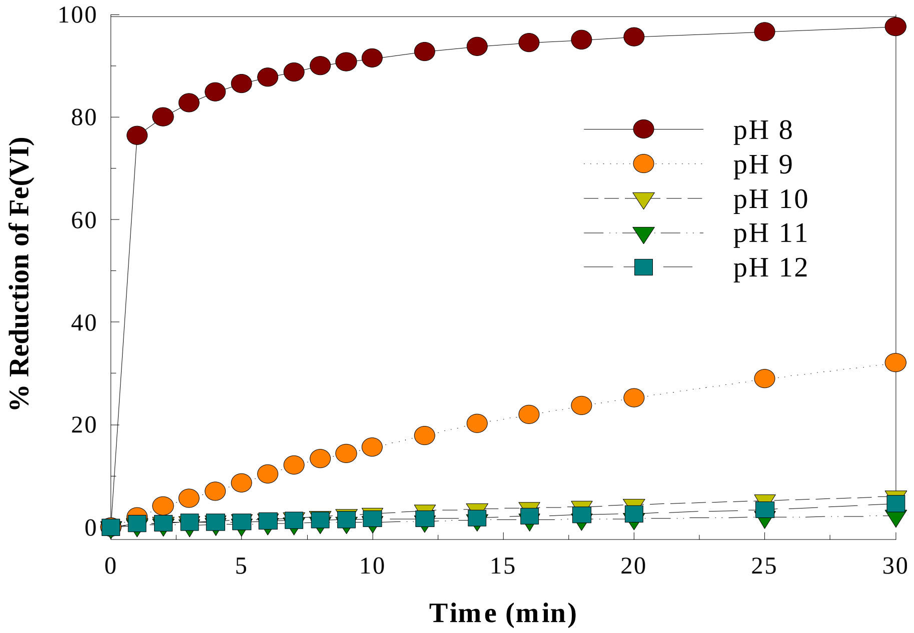


Figure 4.26. *Reduction of Fe(VI) as a function of time for different pH values. [Cd(II)-NTA conc.:5.0 x10^{-4} mol/L and Fe(VI) conc.:1.0x10^{-4} mol/L]*

4.2.5.2. Mineralization of NTA

4.2.5.2.1. Time dependence Study

The mineralization of NTA in the mixed system, i.e., Cd(II)-NTA complex was studied as a function of reaction time at constant pH using TOC data. The basic equation for the decomposition of NTA in the Cd(II)-NTA may be written as equation (4.28):

Fe(VI) + Cd(II)-NTA à Decomplexation of Cd(II)-NTA + Fe(III) à Decomposed NTA Products + Cd(II) + Fe(III) …(4.28)

1.0x10^{-4} mol/L of Cd-NTA was treated with two different dosages of Fe(VI) i.e., 1.0 x10^{-4} and 2.0x10^{-4} mol/L keeping the solution pH~10.0 as constant(phosphate buffer). The TOC values for both of the Fe(VI) treated samples were recorded at regular time intervals for a period of two hours. The recorded TOC values were used to calculate the percent decomposition of NTA which was returned in Figure 4.27. The decomplexation of Cd(II)-NTA was supposed to be very fast step. However, the decomposition of NTA was noted to be slow step. It was clearly shown that the degradation of NTA increases with increasing the contact time and achieved almost a constant value after the 60 min of contact. Further, maximum 23 % of NTA was degraded at the Fe(VI) dosages of $1.0x10^{-4}$ and $2.0x10^{-4}$ mol/L. Quantitatively, within 120 min of contact, the TOC values were decreased from 7.01 mg/L to 5.40 mg/L (for $1.0x10^{-4}$ mol/L of Fe(VI) dosages) and 7.01 mg/L to 5.40 mg/L (for $2.0x10^{-4}$ mol/L of Fe(VI) dosages).It was observed that even an increase in Fe(VI) dose, the degradation of NTA was unaffected which inferred that the 1:1 stoichiometry occurred for the NTA to Fe(VI) independent to the Cd(II) presence. Similarly, in the oxidation of cyanide with Fe(VI), 1:1 stoichiometry was obtained as up to *ca* 1:1 stoichiometry, the percent oxidation of cyanide was almost 100% and beyond that it was decreased (Tiwari *et al.,* 2006)

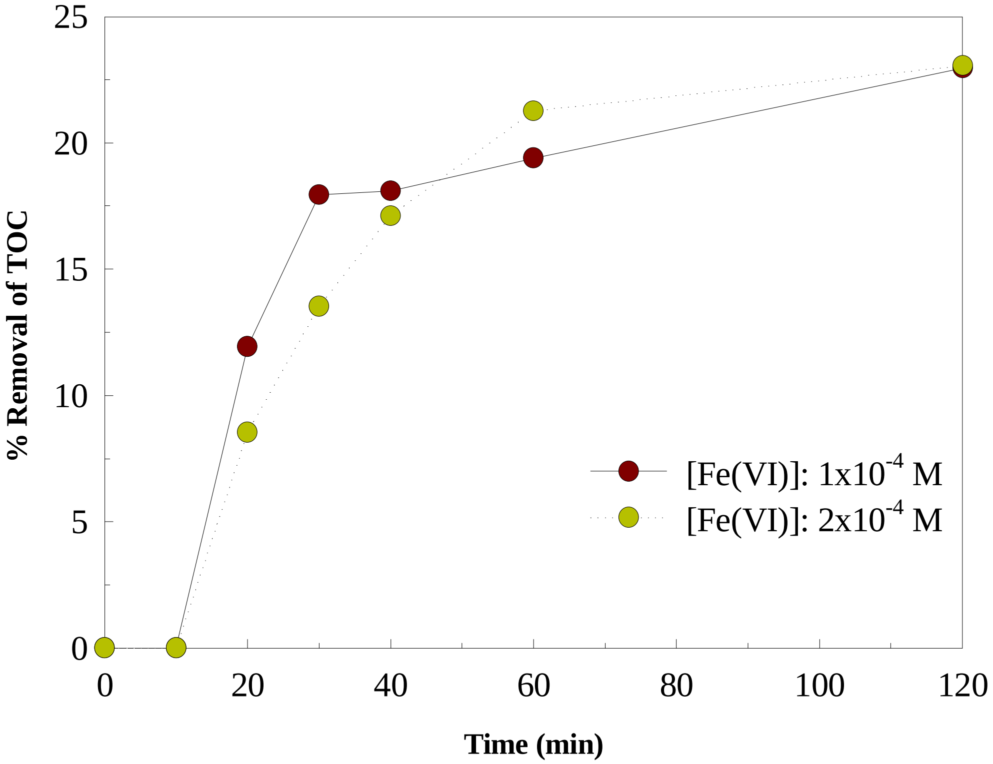


Figure 4.27. *Percent degradation of NTA in the complexed system of Cd(II)-NTA as a function of time [Cd(II)-NTA: 1.0x10^{-4} mol/L; pH:10.0]*

4.2.5.3. Simultaneous Removal of Cd(II)

4.2.5.3.1. Time dependence study

Further removal of Cd(II) following the degradation of Cd(II)-NTA complex by Fe(VI)was studied by analyzing the total cadmium content of the sample solutions before and after treatment with Fe(VI) using an inductively coupled plasma (Optima 2000 DV, Perkin-Elmer, USA). Again, two different doses of Fe (VI), i.e., 1.0 x10^{-4}mol/Land 2.0 x10^{-4} mol/L were used to treat a constant dose of Cd(II)-NTA, i.e., 1.0×10^{-4}mol/L at constant pH 10.0. The treated solutions were constantly stirred in reaction reactors. The aliquots were taken out at regular time intervals within 2 hours, filtered quickly using 0.45 µm syringe filter and subjected to the Cd(II) concentration using ICP. The untreated sample solutions were also simultaneously analyzed to assess the initial concentration of Cd(II). From the obtained data, the percent removal of Cd(II) was calculated for each interval of time. The results obtained were shown in figure 4.28 which indicates that very fast removal of cadmium by Fe(VI) occurred as within few minutes of contact, maximum cadmium was removed confirming the potentiality of Fe(VI) to act as an effective coagulant/adsorbent in wastewater treatment that could efficiently remove the free cadmium from aqueous solutions. At pH 10.0, the free cadmium was presumed to be precipitated as insoluble $Cd(OH)_2$and resulted in the decrease in cadmium concentration in the bulk solution. Further, the ICP results demonstrated that increasing the dosages of Fe(VI) from 1.0 $x10^{-4}$ mol/L to 2.0 $x10^{-4}$ mol/L apparently increased the removal of Cd(II) respectively from 14.9 to 23.8%. Previously, it was observed that maximum of *Ca.* 23% of TOC was removed which was unaffected with the Fe(VI) dose. However, the simultaneous removal of Cd(II) from aqueous solutions was greatly affected with Fe(VI) dose. This increase in percent removal of Cd(II) from aqueous solution may be explicable on the basis of that increasing the dose of Fe(VI) caused an increased concentration of Fe(III) in the solution which may enable for enhanced free Cd(II) removal either by the coagulation/adsorption process. Metal ions such as Mn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+} and Hg^{2+} have been reportedly removed from aqueous solutions via oxidation / coagulation /adsorption process using lower dose of Fe(VI) 10 -100 mg/L (Bartzatt *et al.,* 1992).

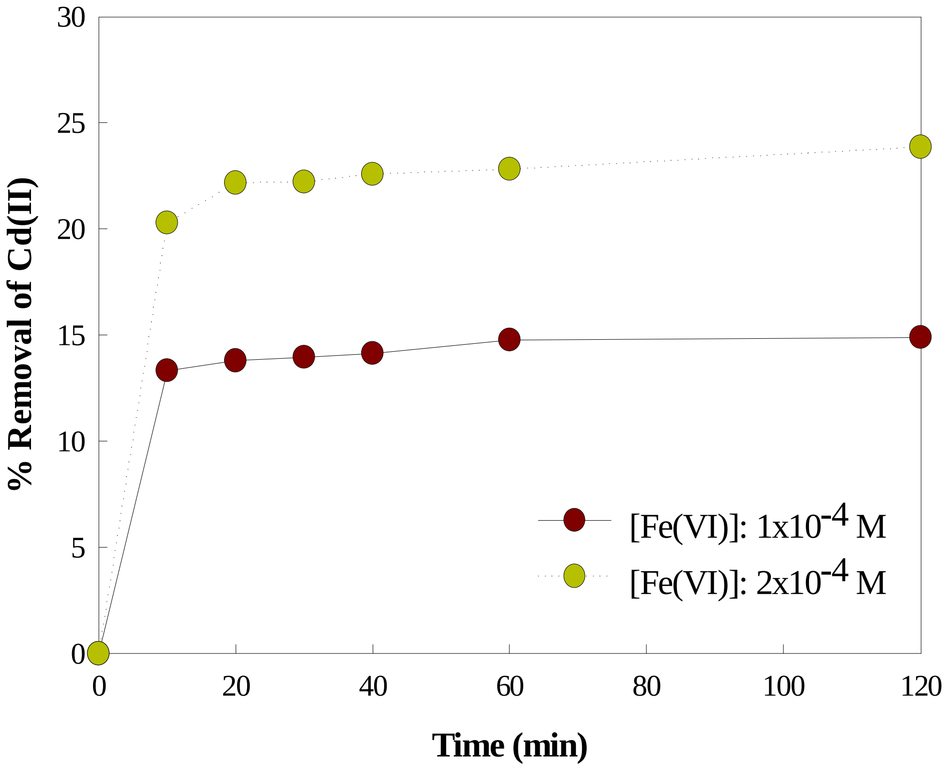


Figure 4.28. *Percent removal of free cadmium as a function of time for two different dosages of Fe(VI) at pH 10.0 [Cd(II)-NTA conc. : 1.0×10^{-4} mol/L]*

4.2.6. Cd(II)-EDTA System

4.2.6.1. Decomplexation and degradation of Cd(II)-EDTA complex species

4.2.6.1.1. Effect of Cd(II)-EDTA Concentration

The study of the degradation of metal complex systems as a function of molar concentration of the metal complex was repeated for the system of Cd(II)-EDTA at different pH conditions, i.e., pH 8.0, 9.0,10.0 and 12.0. The varied molar concentrations of Cd(II)-EDTA, i.e., 0.5, 1.0, 10.0 and 15.0 mmol/L were treated with a constant dose of Fe(VI), 1.0 mmol/L. The treated sample solutions were analyzed using UV-Visible spectrophotometer to observe the change in absorbance of the solution at 510nm at regular intervals of time for a period of 20 mins. Further, the absorbance values were converted into Fe(VI) concentration with usual blank corrections and was represented graphically in Figures 4.29(a) to 4.29(d). From the figures it was evident that fairly significant removal of Fe(VI) occurred in presence of Cd(II)-EDTA. Moreover, an increase in the concentration of Cd(II)-EDTA caused to enhance the decomposition of Fe(VI) indicating that more and more of Cd(II)-EDTA was decomplexed/degraded in solution studied at constant dose of Fe(VI). It was also observed that the removal of Fe(VI), perhaps the degradation of Cd(II)-EDTA, was favored at lower pH values. For example, at pH 8.0, the Fe(VI) was removed as high as 41.59% within 20 mins of contact time whereas it was removed only by 5.0% at pH 12.0 within the same period of contact time employing the Cd(II)-EDTA concentration of 15.0 mmol/L at constant dose of Fe(VI).The results once again reaffirmed the higher reactivity of Fe(VI) at lower pH as cited previously.

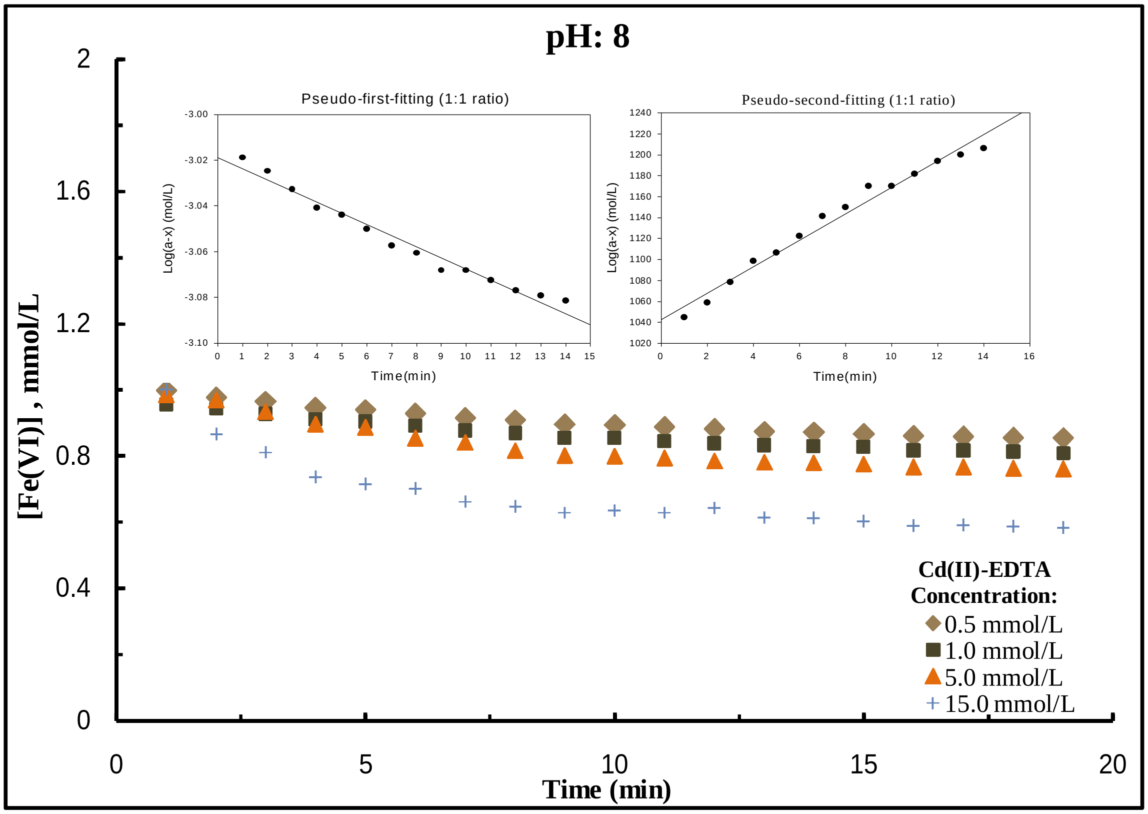


Figure 4.29(a). *Degradation of EDTA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-EDTA at constant pH:8.0. [Initial conc. of Fe(VI): 1.0 mmol/L]*

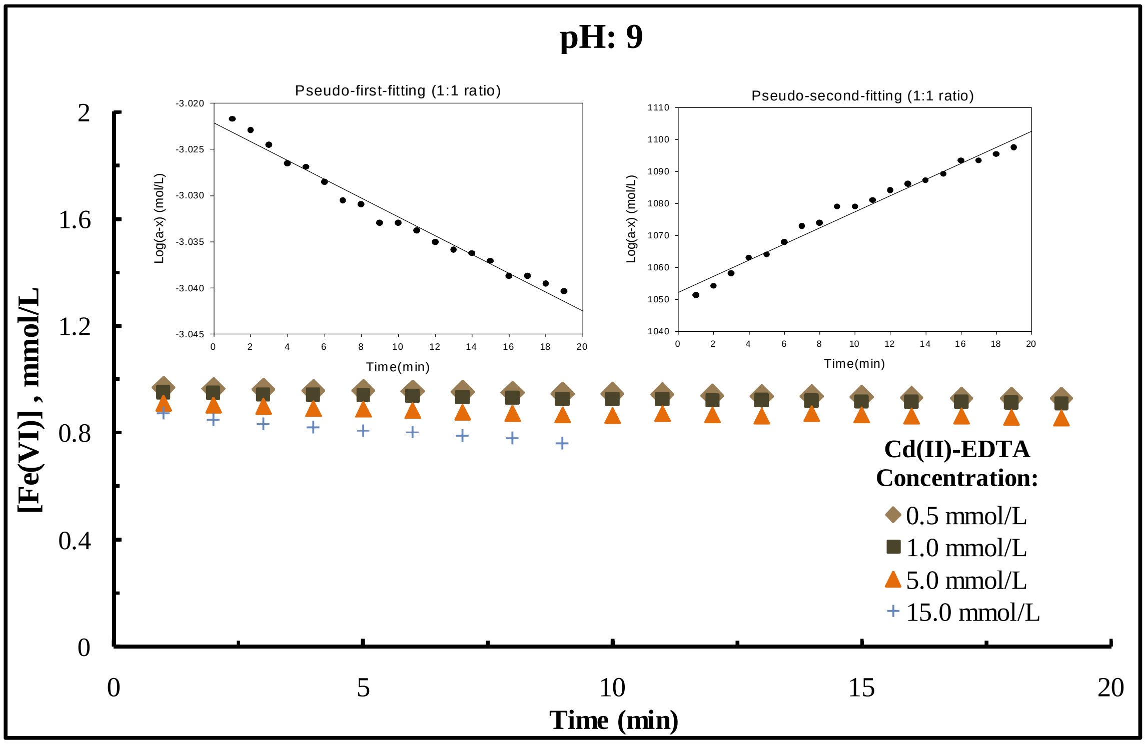


Figure 4.29(b). *Degradation of EDTA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-EDTA at constant pH:9.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

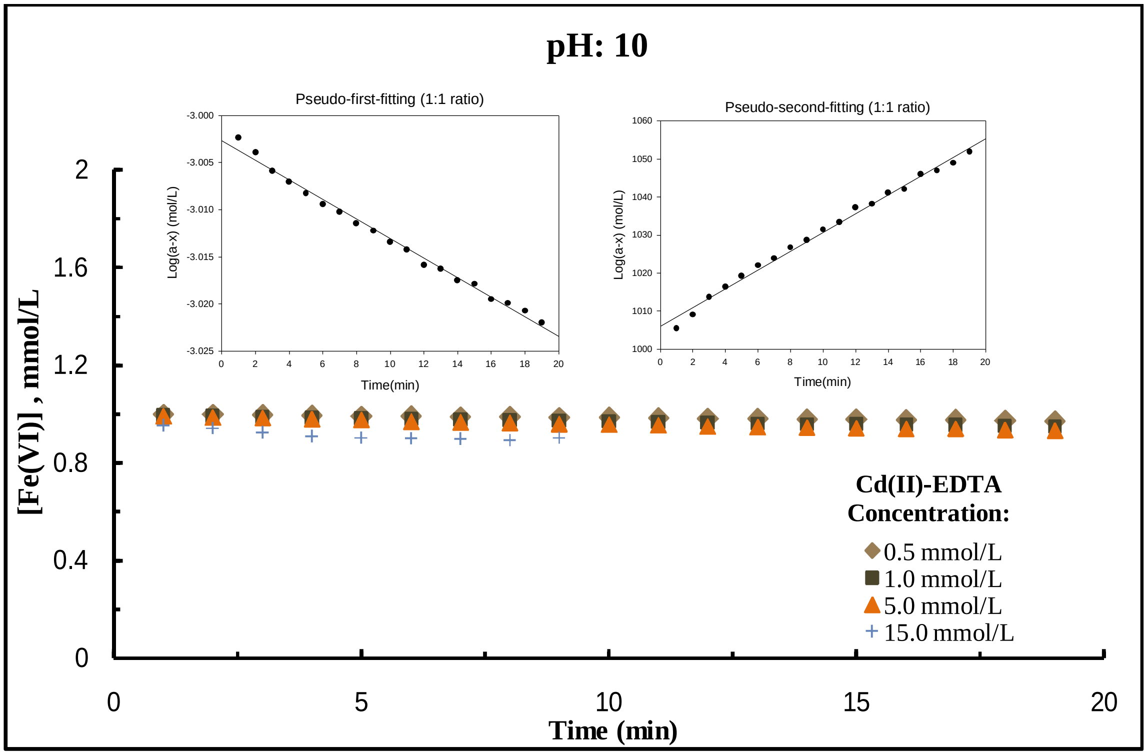


Figure 4.29(c). *Degradation of EDTA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-EDTA at constant pH:10.0. [Initial conc.of Fe(VI): 1.0 mmol/L]*

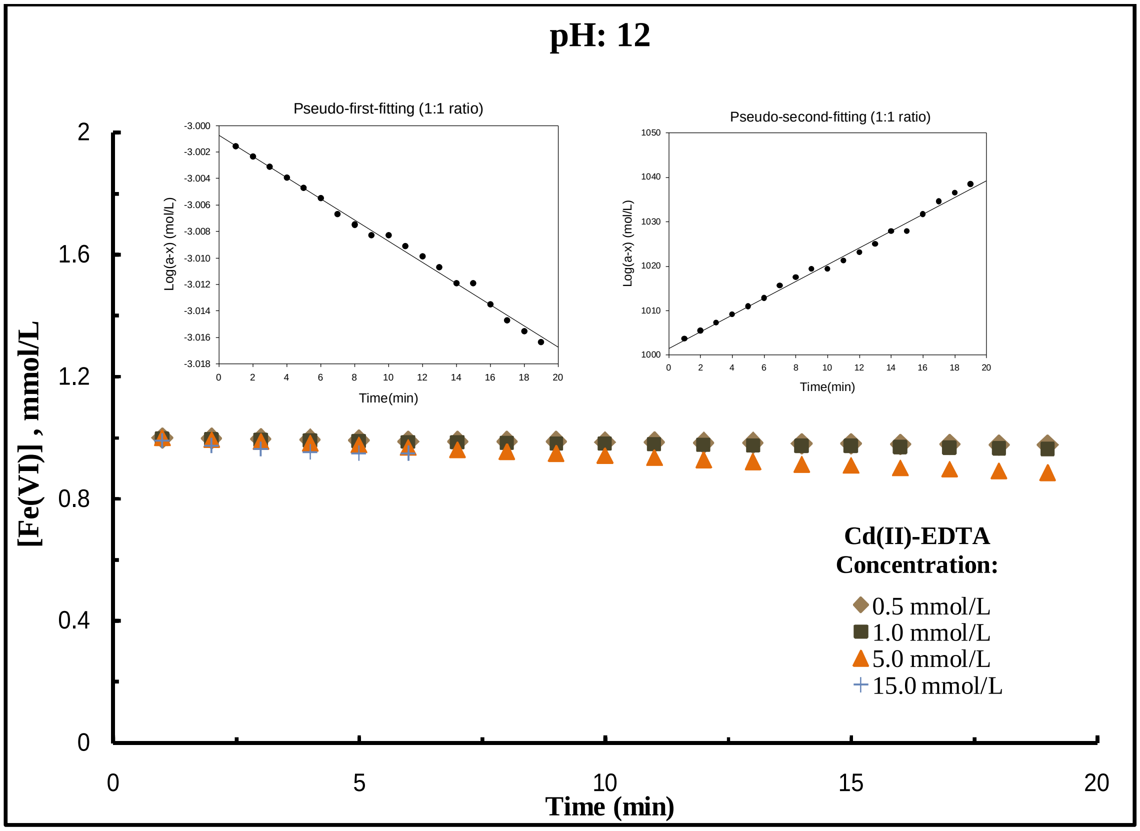


Figure 4.29(d). *Degradation of EDTA in presence of Fe(VI) as a function of time for different conc. of Cd(II)-EDTA at constant pH:12.0. [Initial conc. of Fe(VI): 1.0 mmol/L]*

4.2.6.1.2. Kinetics of Cd(II)-EDTA decomplexation/degradation

Similar to the previous systems, the kinetics of the oxidation of Cd(II)-EDTA by Fe(VI) was again attempted with first and second order rate kinetics with respect to the rate expression assumed as:

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\ [Cd(II) - EDTA]^n \qquad \dots (4.29)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1 \times [Fe(VI)]^m \qquad \dots (4.30)$$

where $k_1 = k[EDTA]^n$ … (4.31)

The insets in figures 4.29(a), 4.29(b), 4.29(c) and 4.29(d) represented the fitting results of pseudo-first and pseudo-second order equations, respectively for pH 8.0, 9.0, 10.0 and 12.0 having the 1:1 Fe(VI) and Cu(II)-EDTA molar stoichiometry. The rate constant values were obtained for both the pseudo-first and psudo-second order rate equations at all varied molar ratios at different pH values. Further, the rate constant values were returned in Table 4.20 along with the R^2 values. Results clearly inferred that the rate constants was decreased significantly with the increase in pH i.e., pH from 8.0 to 12.0 which clearly indicated that the rate of decomposition of Fe(VI) or the degradation of Cd(II)-EDTA was more pronounced at lower pH conditions. Quantitatively, decreasing the pH from 10.0 to 8.0 the rate constant was increased, respectively from 0.23×10^{-2} to 1.84×10^{-2} min^{-1} (for pseudo-first-order) and from 3.80 to 16.28 L/mol/min (for pseudo-second-order) at the 1:1 molar ratios of Fe(VI) and Cd(II)-EDTA.

Table 4.20. *Pseudo-first and Pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentration of Cd(II)-EDTA at different pH conditions.*

Cd(II)-EDTA mmol/L	**Pseudo-first-order rate constant (x10^{-2}) (1/min)**								**Pseudo-second-order rate constant (L/mol/min)**							
	pH 8.0		**pH 9.0**		**pH 10.0**		**pH 12.0**		**pH 8.0**		**pH 9.0**		**pH 10.0**		**pH 12.0**	
	k_1	**R^2**	**k_1**		**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	0.90	0.973	0.23	0.977	0.23	0.992	0.00	0.991	12.62	0.978	2.932	0.979	2.683	0.992	2.683	0.992
1.0	1.84	0.940	0.46	0.987	0.23	0.990	0.23	0.988	16.28	0.890	5.665	0.985	3.802	0.990	3.802	0.99
5.0	6.22	0.920	1.61	0.955	1.38	0.988	0.92	0.989	32.47	0.830	14.59	0.935	80.92	0.988	80.92	0.988
10.0	0.60	0.947	0.23	0.986	0.00	0.990	0.00	0.99	9.08	0.960	2.52	0.987	1.619	0.990	1.619	0.990

The overall rate constant 'k' was again estimated using the rate constants, k_1 obtained for both pseudo-first-order as well as the pseudo-second-order rate law. The value of 'n' was again estimated for 1 and 2; it was best fitted for n=1; since the data was fairly fitted well to the pseudo-first-order rate constant values (*cf* Figure 4-30). The overall rate constant values along with the R^2 values, estimated using the pseudo-first-order rate constant values at different pH values are as shown in Table 4.21. In general increasing the pH, the overall rate constant was decreased. It was also observed that the degradation of Cd(II)-EDTA was almost insignificant at pH values 10.0 and 12.0 hence, was not evaluated.

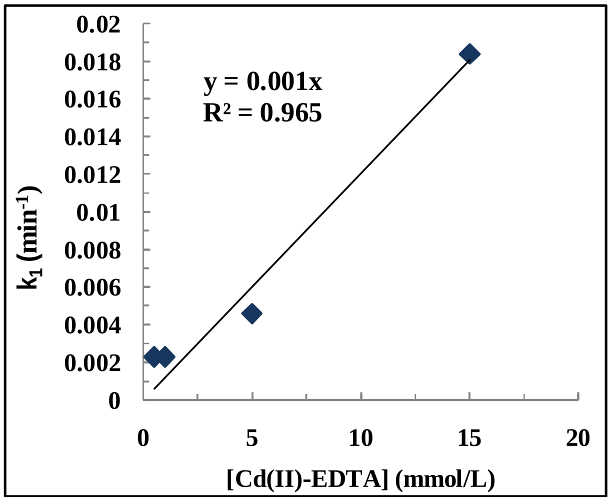


Figure 4.30. *Fitting of pseudo-first-order rate constant values for the degradation of Fe(VI) in presence of different concentrations of Cd(II)-EDTA at pH 9.0.*

Table 4.21. *Overall rate constant in the decomplexation/degradation of Cd(II)-EDTA by ferrate(VI) at different pH conditions*

pH	Cd(II)-EDTA System	
	k (L/mol/min)	**R^2**
8	4.0	0.972
9	1.0	0.960
10	*	*
12	*	*

* *At this pH the* degradation *of Cd(II)-EDTA was almost insignificant*

4.2.6.2. Mineralization of EDTA

The total organic carbon data was further utilized to assess the mineralization of EDTA in the Fe(VI) treated samples of Cd(II)-EDTA. The TOC values were obtained for the treated samples of varied molar ratios of Fe(VI) and Cd(II)-EDTA (1:0.5, 1:1, 1:5, 1:15) at different pH values i.e., pH 8.0, 9.0, 10.0 and 12.0. The results were presented in the form of percent removal of TOC and were shown in Table 4.22 and graphically represented in Figure 4.31.

The results indicated that organic component present in the solutions i.e., EDTA were fairly oxidized by Fe(VI) treatment. Further, higher the percent removal of TOC was observed at lower concentrations of Cd(II)-EDTA for the constant dose of Fe(VI). Decreasing the concentration of Cd(II)-EDTA from 15.0 to 0.50 mmol/L, the corresponding increase in percent removal of TOC was found to be from 5.97% to 35.82% at pH 8.0. It was also observed that the lower pH favored significantly the degradation of EDTA which was markedly suppressed at higher pH. For example, at pH 12.0, the increase in percent TOC removal was only from 2.86% to 13.33 % in decreasing the concentration from 15.0 to 0.50 mmol/L. These results inferred that Fe(VI) showed enhanced reactivity at lower pH conditions.

Table 4.22. *Removal of EDTA from Cd(II)-EDTA complexes by Fe(VI) at different pH values*

pH	% Mineralization of EDTA by Ferrate(VI)			
	Fe(VI) : [Cd(II)-EDTA]			
	1:0.5	**1:01**	**1:05**	**1:15**
8	35.82	24.21	6.84	5.97
9	31.97	22.64	6.64	5.19
10	27.45	20.79	5.31	4.48
12	13.33	18.80	5.28	2.86

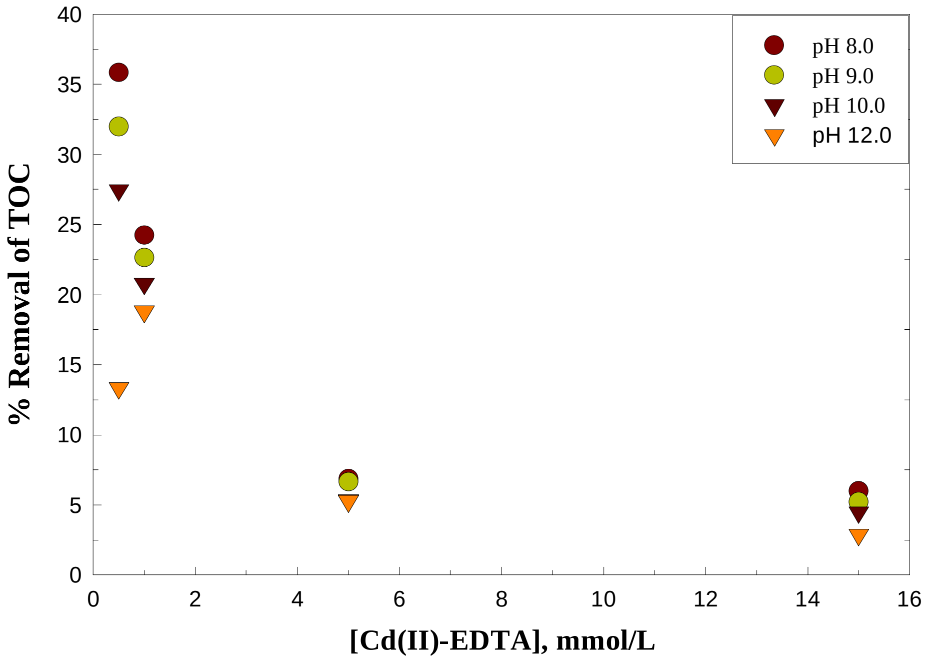


Figure 4.31. *Degradation of EDTA for different concentrations of Cd(II)-EDTA treated with Fe(VI):1.0 mmol/L at different pH values*

4.2.6.3. Simultaneous removal of Cd(II)

The coagulating property of Fe(VI) was exploited further to study the simultaneous removal of Cd(II) from the Fe(VI) treated samples. The removal of Cd(II) was obtained; analyzing the treated and filtered samples at the treated pH as well at the higher pH i.e., at pH 12.0 by raising the solution pH 12.0 with the drop wise addition of conc. NaOH solution. The percent removal of Cd(II) for different concentrations of Cd(II)-EDTA and at different pH values was shown in Table 4.23 and also presented graphically in Figures 4.32. The figure indicates that partial removal of these metal ions occurred at the lower pH values, however, very high percent removal of Cd(II) was observed when the treated sample pH was raised to pH 12.0. Complete removal of Cd(II) ions occurred for the lower concentration of Cd(II)-EDTA, i.e., 0.5 mmol/L when the pH was raised to 12.0 indicating that the decomplexed

Cd(II) was coagulated significantly at higher pH values. It was also observed that the coagulation was suppressed significantly at lower pH conditions.

Table 4.23. *Percent Removal of Cd(II) by Fe(VI) for different molar ratio of Cd(II)-EDTA and Fe(VI) at different pH values [Initial concentration of Fe(VI): 1.0 mmol/L]*

Fe(VI): Cd(II)-EDTA	**% Removal of Cd(II) by Fe(VI)**						
	pH 8.0	**Raised to pH 12.0**	**pH 9.0**	**Raised to pH 12.0**	**pH 10.0**	**Raised to pH 12.0**	**pH12.0**
1:0.5	5.20	100.00	10.89	100.00	45.69	100.00	100
1:01	4.80	58.40	5.80	39.65	20.00	45.37	36.85
1:10	2.50	30.50	3.8	11.23	8.9	7.55	10.2
1:15	1.03	12.30	0.5	4.50	1.2	2.10	5.9

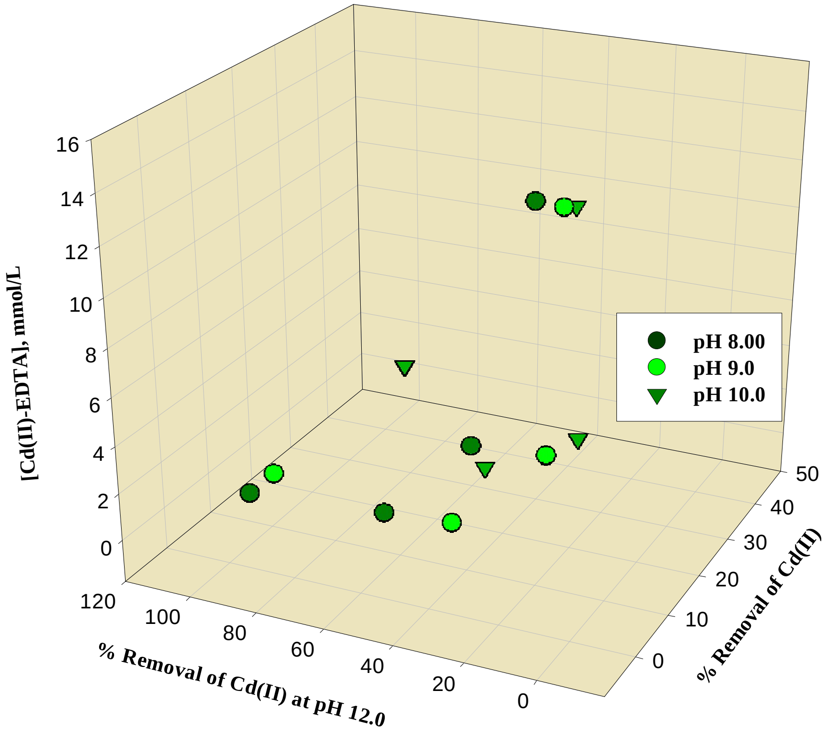


Figure 4.32. *Simultaneous removal of Cd(II) for different concentrations of Cd(II)-EDTA treated with Fe(VI): 1.0 mmol/L at different pH values*

4.2.7. Zn(II)-IDA system

4.2.7.1. Decomplexation and degradation of Zn(II)-IDA complex species

4.2.7.1.1. Effect of Zn(II)-IDA Concentration

The decomplexation and degradation of Zn(II)-IDA complexes was investigated for different molar ratios of Zn(II)-IDA, 0.3:1 to 15:1 keeping the initial concentration of Fe(VI) constant at 1.0 mmol/L and at different pH conditions (pH 8.0 to pH 12.0). The results obtained were shown graphically in Figures 4.33(a), 4.33(b) and 4.33(c) respectively for pH 8.0, 9.0 and 10.0. Figures showed that a fast decrease/removal of Fe(VI) occurred during the initial period of time, slowed down in the latter stage and reached almost a constant value just after 10 mins of time. This initial fast degradation of IDA was more pronounced as the pH was lowered. At pH 8.0 and 9.0, very fast degradation of Fe(VI) was observed for higher concentrations, i.e., 5.0 and 10.0 mmol/L of Zn(II)-IDA solution attained more than 80 % removal of Fe(VI) just within 5 mins of contact time. It was further noted that increasing the molar concentration of Zn(II)-IDA generally caused to enhance the decomplexation /degradation of Zn(II)-IDA species in solutions as more and more Fe(VI) was decomposed with higher rates. As we increase the concentration of Zn(II)-IDA from 0.3 to 5.0 mmol/L, the percent decomposition of Fe(VI) was increased from ~57% to 88% at pH 8.0. These results inferred that even the enhanced level of pollutant concentration i.e., Zn(II)-IDA in wastewater could be effectively treated with the regulated dose of Fe(VI) .

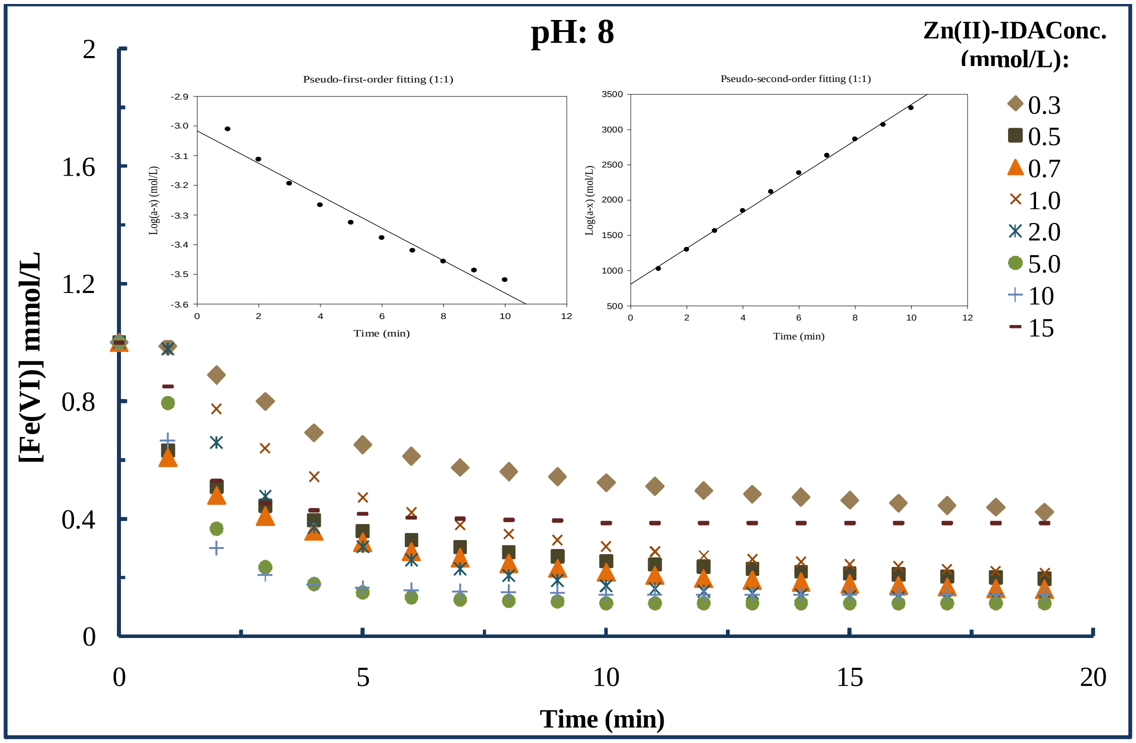


Figure 4.33(a). *Degradation of IDA in presence of Fe(VI) as a function of time for different conc. of Zn(II)-IDA at constant pH:8.0. [Initial conc. of Fe(VI):1.0 mmol/L]*

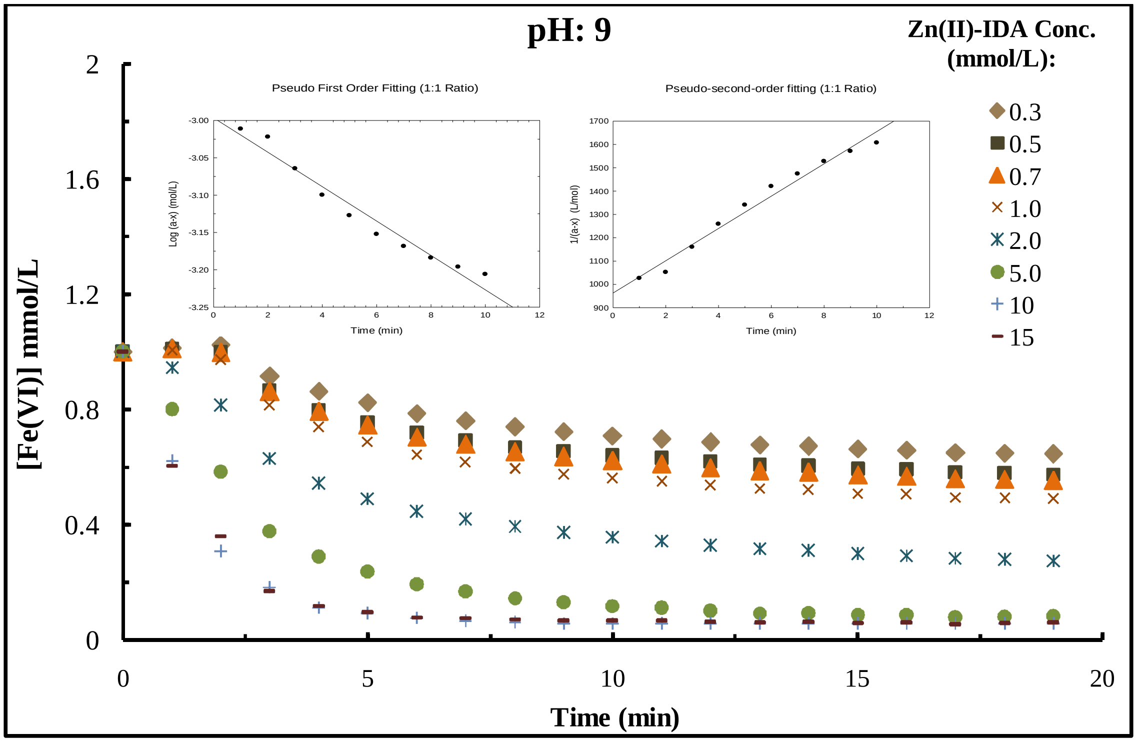


Figure 4.33(b). *Degradation of IDA in presence of Fe(VI) as a function of time for different conc. of Zn(II)-IDA at constant pH:9.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

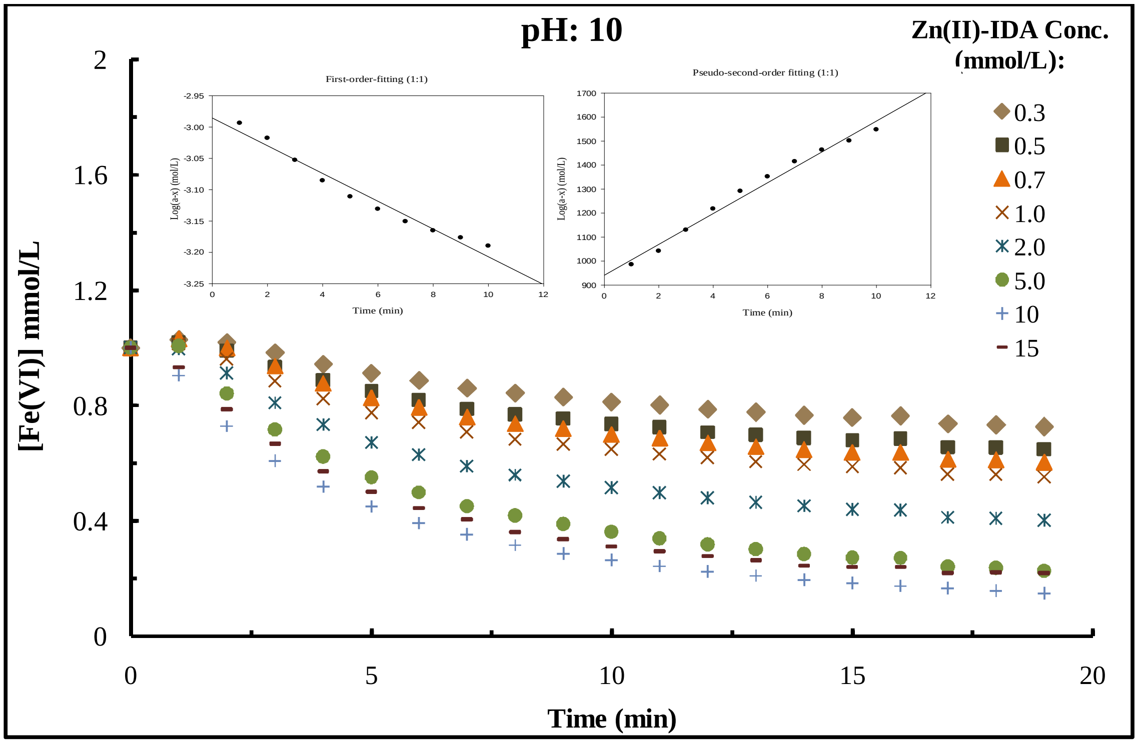


Figure 4.33(c). *Degradation of IDA in presence of Fe(VI) as a function of time for different conc. of Zn(II)-IDA at constant pH:10.0. [Initial conc. of Fe(VI): 1.0 mmol/L]*

4.2.7.1.2. Kinetics of Zn(II)-IDA decomplexation/degradation

The simple irreversible reactions were used in the kinetic study of the oxidation of the complexed species Zn(II)-IDA by the Fe(VI). Hence, decomplexation of Zn(II)-IDA be expressed by the following equations:

$$\text{Fe(VI)} + \text{Zn(II)-IDA} \rightarrow \text{Fe(III)} + \text{Oxidized Products} + CO_2 + N_2 \qquad \ldots (4.32)$$

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Zn(II) - IDA]^n \qquad \ldots (4.33)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)]^m \qquad \ldots (4.34)$$

$$k_1 = k\,[\text{Zn(II)-IDA}]^n \qquad \ldots (4.35)$$

The value of k_1 in equation (4.33) was calculated using first order (m=1) as well as second order (m=2) rate laws using the UV-Visible data obtained for different concentrations of

Zn(II)-IDA at different solution pH. The rate constants, k_1 values obtained for both first and second order rate equations were summarized in Table 4.24 and the fittings for 1:1 molar stoichiometry for pH 8.0, 9.0 and 10.0 were presented as insets in Figures 4.33(a) to 4.33(c). Rate constant data obtained clearly implied that the increase in solution pH greatly hampered the removal of Fe(VI) or degradation of Zn(II)-IDA species in solution. Quantitatively, decreasing the pH from 10.0 to 8.0 the rate constant was increased, respectively from 5.09×10^{-2} to 75.07×10^{-2} min^{-1} (for pseudo-first-order) and from 44.6 to 199.62 L/mol/min (for pseudo-second-order) at the 1:1 molar ratios of Fe(VI) and Zn(II)-IDA. Again, the rapid and fast decomposition of ferrate(VI) at lower pH was attributed to the higher redox potential of Fe(VI) at lower pH values (Sharma 2002; Jiang and Lloyd, 2002). It was also noted that, at higher pH, i.e., pH 11.0 and 12.0, the rate of decomposition of Fe(VI) was almost independent with increasing the Zn(II)-IDA concentration (data not included). Moreover, the decomposition rate constant was also found to be significantly low values. This could be explicable with the fact that at very high pH conditions the reactivity of Fe(VI) was decreased greatly; whereas the stability of Fe(VI) was increased significantly at this high pH values .

Table 4.24. *Pseudo-first and Pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentration of Zn(II)-IDA at different pH conditions*

[Zn(II)-IDA] (mmol/L)	Pseudo-first-order rate constant (x10^{-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	4.122	0.888	5.02	0.983	2.28	0.968	69.363	0.949	31.501	0.924	22.859	0.968
0.5	5.735	0.899	6.33	0.979	2.879	0.949	189.95	0.971	40.094	0.909	30.938	0.955
0.7	65.866	0.902	6.73	0.978	3.823	0.958	252.18	0.978	44.393	0.915	38.099	0.959
1.0	75.078	0.896	8.04	0.982	5.09	0.968	199.62	0.979	56.512	0.926	44.682	0.955
2.0	183.549	0.932	12.644	0.945	7.416	0.971	413.90	0.971	138.84	0.955	82.146	0.977
5.0	495.370	0.951	263.92	0.969	13.242	0.987	842.37	0.912	678.60	0.974	189.38	0.997
10.0	-	-	564.46	0.996	17.111	0.991	-	-	2053.8	0.982	311.54	0.998
15.0	-	-	554.10	0.992	-	-	-	-	1917.0	0.929	-	-

The overall rate constant ‘k’ was estimated using the k_1 values (obtained by pseudo-first-order rate constant values as well the pseudo-second-order rate constant). It was observed that the value of ‘n’ which was estimated for 1 and 2; best fitted for n=1; since the data was fairly fitted well to the pseudo-first-order rate constant values (*cf* 4-34). Therefore, using the pseudo-first-order rate constant values, the overall rate constant values along with the R^2 values were estimated at different pH values and returned in table 4.25. In general, increasing the pH, the overall rate constant was decreased. The overall rate constant is found to be decreased from 97.42 to 29.49 L/mol/min as pH is increased from 8.0 to 10.0, again to be noted in accordance to the reactivity of the ferrate(VI) in solution since the protonated ferrate species ($HFeO_4^- \leftrightarrow H^+ + FeO_4^{2}$; $pK_a^2=7.3$) possessed with larger spin density than the deprotonated species (Ohta *et al.*,2001; Sharma *et al.*, 2004). It was also clearly demonstrated that 1:1 stoichiometry was occurred in the decomplexation/degradation of Zn(II)-IDA with ferrate(VI).Sharma *et al.*,*(*2002) also reported a stoichiometry of 1:1 for Fe(VI) :SMX and that the Fe(VI) oxidation of thiocyanate was well expressed by first-order with respect to Fe(VI) under pseudo-first order conditions with SCN in excess.

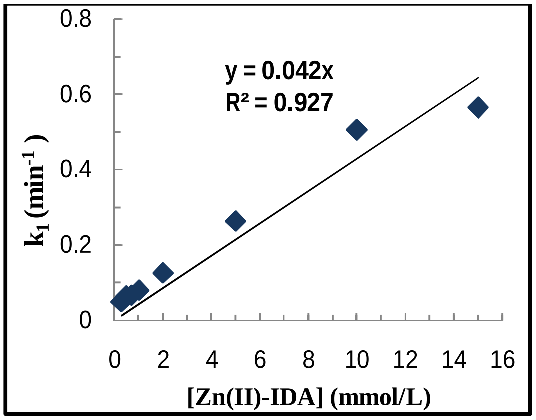


Figure 4.34. *Fitting of pseudo-first-order rate constant values for the degradation of Fe(VI) in presence of different concentrations of Zn(II)-IDA at pH 9.0.*

Table 4.25. *Overall rate constant in the decomplexation/degradation of Zn(II)-IDA by ferrate(VI) at different pH conditions*

pH	**Zn(II)-IDA System**	
	k (L/mol/min)	**R^2**
8.0	97.42	0.993
9.0	42.91	0.928
10.0	29.49	0.806

4.2.7.2. Mineralization of IDA

The degradation of IDA following the decomplexation of Zn(II)-IDA complexes by Fe(VI) was studied by obtaining the total organic carbon data for the varied stoichiometric ratios of Fe(VI) and Zn(II)-IDA treated at various pH conditions i.e., pH 8.0 to 12.0. These results as shown in Table 4.26 and graphically represented in Figure 4.35 demonstrated that higher percent of IDA was mineralized/degraded at lower concentrations of Zn(II)-IDA complex species using a constant dose of Fe(VI). Decreasing the concentration of Zn(II)-IDA from 15.0 to 0.30 mmol/L, the corresponding increase in percent removal of TOC was recorded from 14.59 to 52.61% at pH 8.0. These results demonstrated that an enhanced percent of IDA was degraded at lower IDA concentrations for a constant dose of Fe(VI). The higher degree of the degradation of IDA at lower pH values indicated the higher stability of Fe(VI) at highly alkaline conditions.

Table 4.26. *Mineralization of IDA from Zn(II)-IDA complex species by Fe(VI) at different pH values*

pH	**% Mineralization of IDA by Ferrate(VI) treatment**							
	Fe(VI) : [Zn(II)-IDA]							
	1: 0.3	**1: 0.5**	**1: 0.7**	**1: 1**	**1: 2**	**1: 5**	**1:10**	**1:15**
8	52.61	45.82	42.86	46.67	45.31	39.80	21.27	14.59
9	52.14	41.74	42.79	45.83	45.04	35.61	21.10	13.42
10	41.83	35.29	41.24	42.15	44.60	34.59	20.34	10.32
11	41.71	26.92	34.89	40.29	43.66	29.39	17.74	9.34
12	40.01	25.25	28.84	36.13	30.67	21.35	14.67	11.57

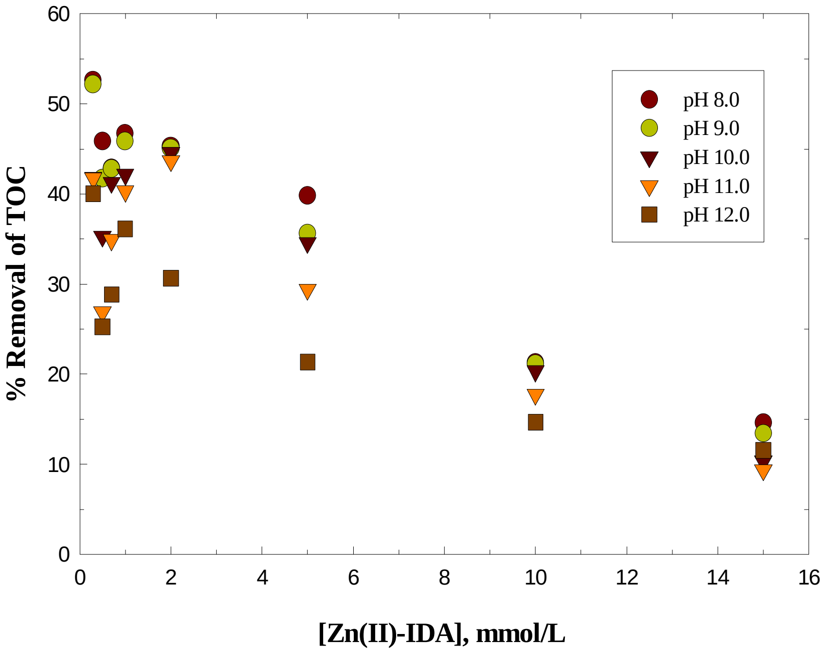


Figure 4.35. *Degradation of IDA for different concentrations of Zn(II)-IDA treated with Fe(VI):1.0x10*$^{-3}$*mol/Lat different pH values*

4.2.7.3. Simultaneous Removal of Zn(II)

Simultaneous removal of Zn(II) ions from the treated solutions of Zn(II)-IDA by Fe(VI) through coagulation/adsorption was investigated using the AAS data. The removal of Zn(II) was obtained; analyzing the treated and filtered samples at the treated pH as well at the higher pH i.e., at pH 12.0 obtained by raising the solution pH 12.0 using conc. NaOH solution. The percent of Zn(II) removal was presented in Table 4.27 and also graphically in Figure 4.36. These data showed that partial removal of Zn(II) ions occurred at the lower pH values however, a significant increase in percent removal of Zn(II) was obtained by raising the solution pH to 12.0. These results, perhaps, indicated that the Zn(II)-IDA species treated at various pH values were decomplexed completely and the mineralization of IDA occurred partly. More than 90% of Zn(II) was removal at pH 12.0 which inferred that decomplexed Zn(II) was coagulated significantly at elevated pH value i.e., at pH 12.0. An insignificant removal of Zn(II) by Fe(VI) at lower pH was also otherwise reported in literature (Jiang and Lloyd, 2002)

Table 4.27. *Percent Removal of Zn(II) by Fe(VI) for different molar ratio of Zn(II)-IDA and Fe(VI) at different pH values [Initial concentration of Fe(VI): 1.0x10^{-3}mol/L]*

Fe(VI): Zn(II)-IDA	**% Removal of Zn(II) by Fe(VI)**								
	pH 8.0	**Raised to pH 12.0**	**pH 9.0**	**Raised to pH 12.0**	**pH 10.0**	**Raised to pH 12.0**	**pH 11.0**	**Raised to pH12.0**	**pH 12.0**
1:03	26.83	96.00	25.40	95.00	7.41	90.40	62.50	98.55	90.32
1:05	11.11	90.86	24.03	94.16	2.13	89.60	58.50	92.50	95.92
1:07	6.06	87.35	10.50	96.72	46.67	90.20	54.00	90.20	95.08
1:1	5.06	70.20	2.73	80.5	44.30	85.50	52.17	89.60	96.25
1:2	4.60	71.60	3.57	40.20	29.33	65.50	30.50	91.67	70.37
1:5	7.30	17.68	0.50	7.46	15.26	30.20	12.78	50.20	94.78
1:10	8.20	10.80	0.34	5.00	7.59	11.00	9.30	30.00	90.03
1:15	6.89	4.93	0.49	0.60	6.58	3.77	7.18	14.83	88.7

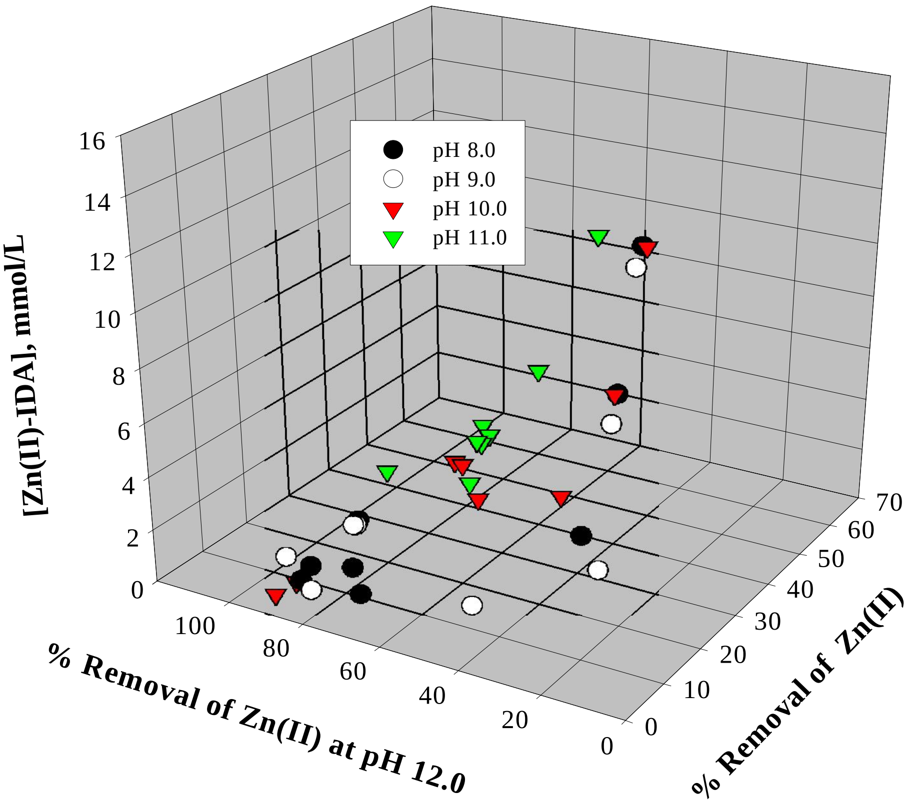


Figure 4.36. *Simultaneous removal of Zn(II) for different concentrations of Zn(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH value*

4.2.8. Zn(II)-NTA system

4.2.8.1. Decomplexation and degradation of Zn(II)-NTA complex species

4.2.8.1.1. Effect of Zn(II)-NTA Concentration

The decomplexation of Zn(II)-NTA was carried out at pH 9.2 with variation of Zn(II)-NTA concentration and the ferrate dose of 1x10^{-4} mol/L.The sample solutions were stirred for 180 mins and then analyzed for the remaining ferrate concentration using UV-Visible spectrophotometer and the results obtained were shown graphically in Figure 4.37.The blank data was obtained in absence of Zn(II)-NTA. A slightly increased removal/degradation of Fe(VI) in this condition could occur perhaps through the self-decomposition of Fe(VI) (Tiwari *et al*., 2007).The results indicated that very fast removal of Fe(VI) occurred within initial contact time for lower concentrations of Fe(VI); just within 20 mins of contact, 100 percent removal of Fe(VI) occurred for the concentration of 1x10^{-2} mol/L of Zn(II)-NTA whereas only about 50% removal of Fe(VI) was observed for lower concentrations of Zn-NTA, i.e., 1x10^{-4} mol/L and 2x10^{-4} mol/L of Zn(II)-NTA after 3 hours of contact. The results are in accordance with the studies conducted on trichloroethylene in which the percent oxidation of trichloroethylene with Fe(VI) was found to be increased considerably with increasing ferrate dosage (DeLuca *et al.*, 1983)

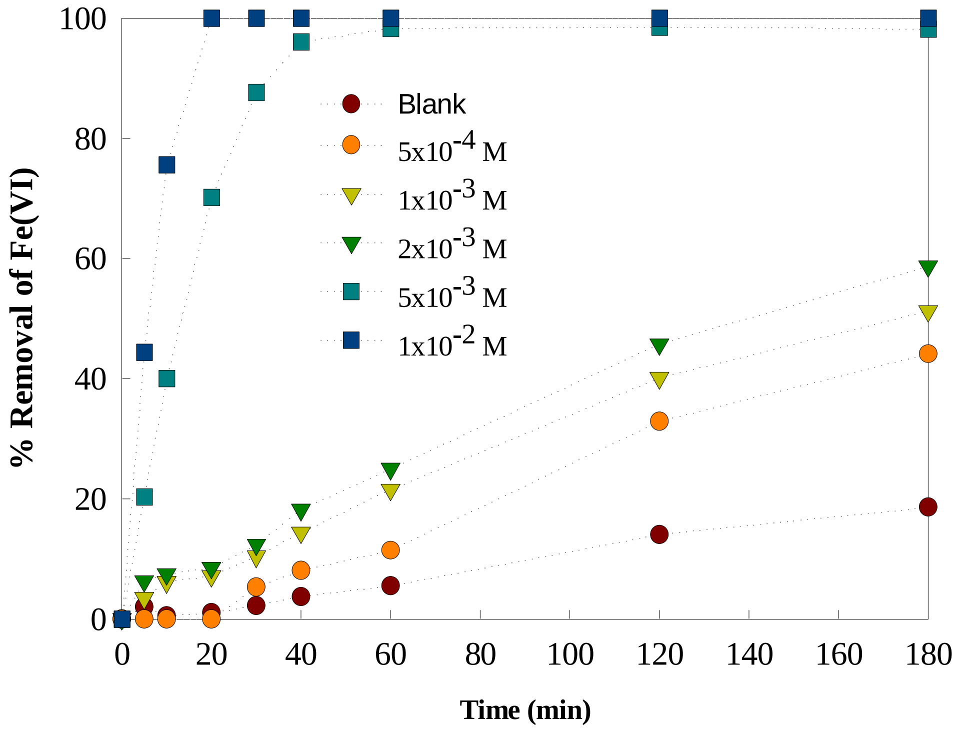


Figure 4.37. *Percent reduction of 1x10^{-4} mol/L Fe(VI) at five different Zn(II)-NTA concentrations as a function of time at pH 9.2.*

4.2.8.1.2. Kinetics of Zn(II)-NTA decomplexation/degradation

Similar to the previous complexed systems under this study, the rate equation for the degradation of Zn(II)-NTA was assumed by the following equations:

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Zn(II)-NTA]^n \qquad \ldots(4.36)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)]^m \qquad \ldots(4.37)$$

$$\text{where } k_1 = k\,[Zn(II)\text{-}NTA]^n \qquad \ldots(4.38)$$

Where k represents the overall rate constant of the reaction (4.36) and the [Fe(VI)] and [Zn(II)-NTA] are the molar concentrations of Fe(VI) and Zn(II)-NTA, respectively, m and n are the orders of the reaction with respect to the each reactant. For all Zn(II)-NTA concentrations, the first-order equation was better described than the second-order equation. Hence, the pseudo-first order degradation of Fe(VI) occurred. From this analysis, m was regarded as 1. The k_1 values at five different Zn(II)-NTA concentrations were summarized in Table 4.28. In order to optimize the value of ‘n’, the k_1 values were fitted with Zn(II)-NTA concentration by assuming n value as 1 or 2. The k_1 values were fitted well for the first-order rate equation (correlation coefficient: 0.981) than the second-order rate equation (correlation coefficient: 0.928). Hence, it was concluded that under the condition stated, the rate of reduction of Fe(VI) in presence of Zn(II)-NTA was first-order for both Fe(VI) and Zn(II)-NTA hence we may write:

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)]^1[Zn(II) - NTA]^1 \qquad \ldots(4.39)$$

and the overall rate constant (k) was found to be 15.2 L/mol/min. The similar observations also reported by Sharma *et al.* (1998b) for the oxidation of un-complexed cyanide with Fe(VI) and reported that the kinetics follows first order rate law to each of the reactant i.e., -d[Fe(VI)]/dt = k[Fe(VI)] $[\text{Cyanide}]_T$. Similarly, Yngard *et al.* (2007) reported the similar first order oxidation of Fe(VI) in presence of $Zn(CN)_4^{2-}$ whereas it was reported half order with respect to the $Zn(CN)_4^{2-}$ complex. Hence, they estimated the overall k ($M^{0.5}\ s^{-1}$) was found to be 3.56±0.13 at pH 9.1.

Table 4.28. *Rate constant (k_1) for the Fe(VI) reduction at five different Zn(II)-NTA Concentrations*

[Zn(II)-NTA] (mol/L)	**k_1 value (min^{-1})**	**Correlation coefficient (First-order)**
$5x10^{-4}$	0.0034	0.9831
$1x10^{-3}$	0.004	0.9965
$2x10^{-3}$	0.0049	0.996
$5x10^{-3}$	0.07	0.9879
$1x10^{-2}$	0.14	0.9907

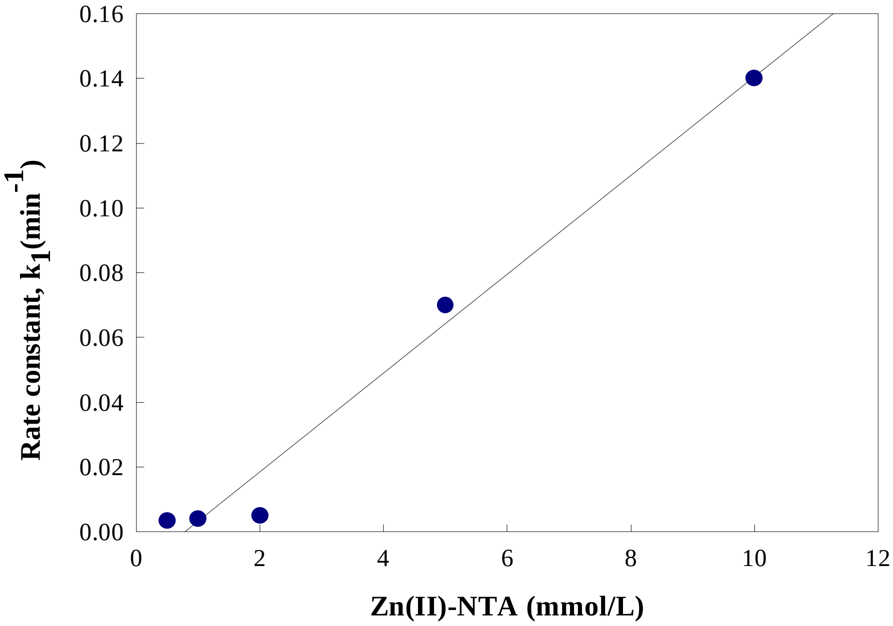


Figure 4.38. *A linear correlation between rate constant (k_1) and Zn(II)-NTA concentration by assuming as 1.*

4.2.9. Ni(II)-IDA system

4.2.9.1. Decomplexation and degradation of Ni(II)-NTA complex species

4.2.9.1.1. Effect of Ni(II)-IDA Concentration

The study of the degradation of metal organic complexes by Fe(VI) was undertaken for Ni(II)-IDA systems. The Fe(VI) removal was observed by the absorbance data obtained by using UV-Visible spectrophotometer. 1.0 mmol/L of Fe(VI) was used to treat different molar solutions of Ni(II)-IDA so as to achieve molar compositions of Fe(VI) and Ni(II)-IDA as 1:03, 1:05,1:07, 1:1, 1:2, and 1:10 and was studied at different pH (8.0, 9.0 and 10.0). The results obtained were represented graphically in Figure 4.39(a) to 4.39(c). The results inferred that Fe(VI) was removed rapidly and significantly in presence of Ni(II)-IDA complexes. This is demonstrated by the fact that Fe(VI) was found to be degraded rapidly in presence of Ni(II)-IDA at the start of reaction and just within *ca*. 5-10 mins of contact time reaches a constant value or gradually slowed down.Within the initial 5 mins, as high as ~ 75% to 95% of Fe(VI) removal occurred for the various molar concentrations of Ni(II)-IDA at pH 8.0.It was further observed that increasing the molar concentration of Ni(II)-IDA generally caused to enhance the decomplexation/degradation of Ni(II)-IDA species in solutions as more and more Fe(VI) was decomposed with a higher rate. For example, at pH 8.0, for the lowest concentration of the sample solution i.e., 0.3 mmol/L, maximum of 92.16% of Fe(VI) was removed within 13 mins of contact time whereas complete reduction of Fe(VI) i.e., 100 % was observed just within 11 mins of contact for the higher concentrations of Ni(II)-IDA i.e., 2.0 mmol/L and above at the same pH 8.0. Increasing the concentration from 0.3 mmol/L to 15.0 mmol/L, the corresponding percent decompostition of Fe(VI) was increased from 64.01 to 99.23 % within 20 mins of contact time at pH 9.0. It is therefore, to be illustrated gain that acidic conditions favoured decomplexation of Ni(II)-IDA complexes in presence of Fe(VI).

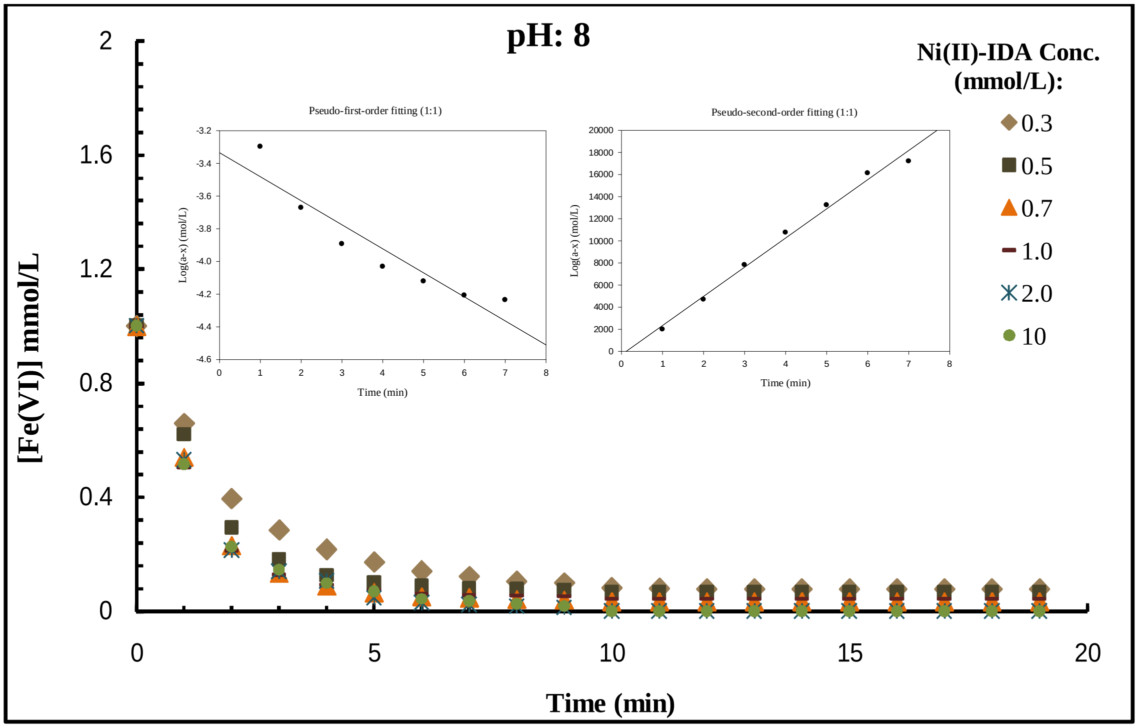


Figure 4.39(a). *Degradation of Fe(VI) as a function of time for different concentrations of Ni(II)-IDA at constant pH:8.0.[Initial conc. of Fe(VI): 10 mmol/L]*

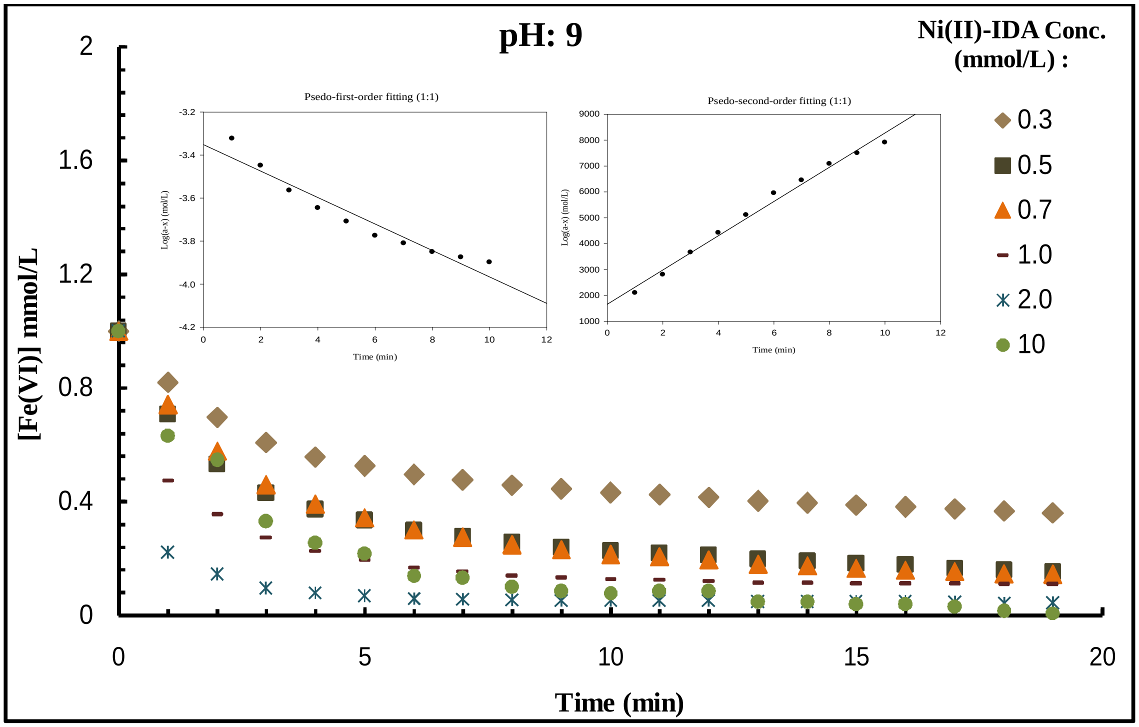


Figure 4.39(b). *Degradation of Fe(VI) as a function of time for different concentrations of Ni(II)-IDA at constant pH:9.0.[Initial conc. of Fe(VI): 1.0 mmol/L]*

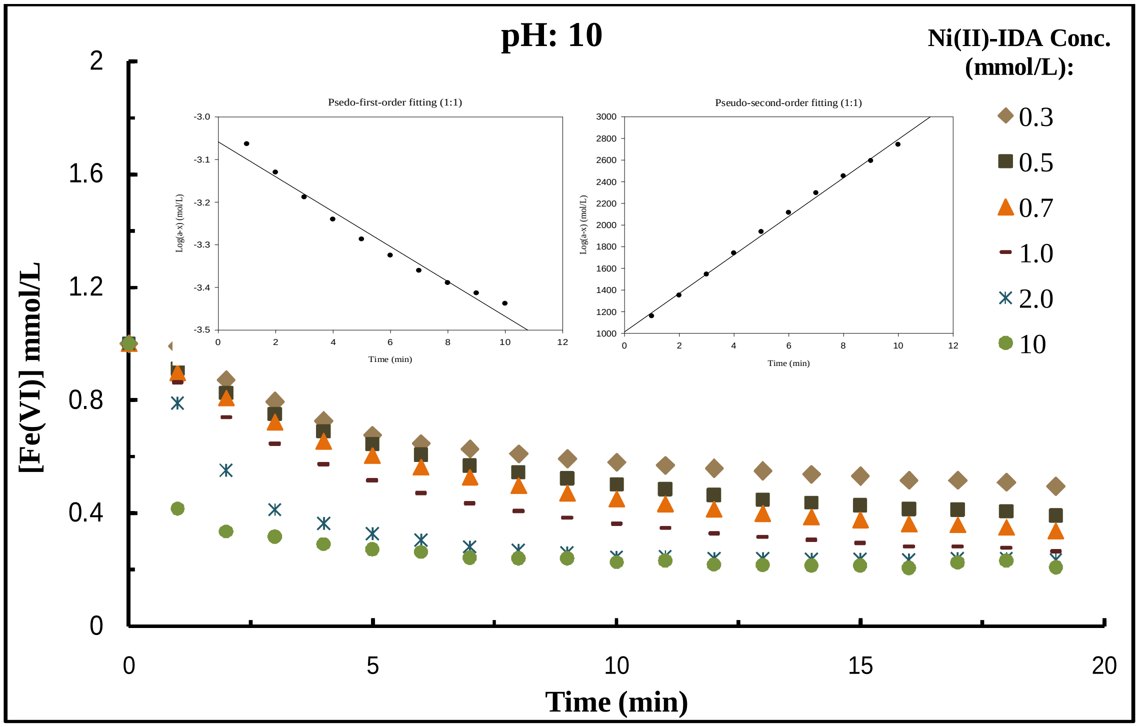


Figure 4.39(c). *Degradation of Fe(VI) as a function of time for different concentrations of Ni(II)-IDA at constant pH:10.0. [Initial conc. of Fe(VI): 1.0 mmol/L]*

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

The kinetic studies were conducted for the complexed systems, the oxidation of Ni(II)-IDA by Fe(VI) was studied with pseudo-first order and pseudo-second order rate laws with respect to the following rate expression assumed to occur for the decomplexation of Ni(II)-IDA:

$$-\frac{d[Fe(VI)]}{dt} = k\,[Fe(VI)]^m\,[Ni(II)-IDA]^n \qquad \ldots(4.40)$$

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)]^m \qquad \ldots(4.41)$$

$$k_1 = k\,[\text{Ni(II)-IDA}]^n \qquad \ldots(4.42)$$

The insets in Figures4.39(a), 4.39(b) and 4.39(c) represent the fitting results of pseudo-first and pseudo-second order equations respectively at pH 8.0, 9.0 and 10.0 having the 1:1 Fe(VI) and Ni(II)-IDA molar stoichiometry. From the rate constant values obtained for first and second order equations (summarized in Table 4.29), it was observed that that the rate constants were decreased significantly with the increase in pH from 8.0 to 10.0 clearly indicated that the rate of decomposition of Fe(VI) or the degradation of Ni(II)-IDA was observed significant at lower pH. Quantitatively, decreasing the pH from 10.0 to 8.0 the rate constant was increased, respectively from 11.28 $x10^{-2}$ to $55.73x10^{-2}$ min^{-1} (for pseudo-first-order) and from 143.2 to 2640.0 L/mol/min (for pseudo-second-order) at the 1:1 molar ratios of Fe(VI) and Ni(II)-IDA, which demonstrated the higher reactivity of Fe(VI) at lower pH due to its increased redox potential at acidic conditions.

Table 4.29. *Pseudo-first and Pseudo-second order rate constants obtained for the degradation of ferrate(VI) using various concentration of Ni(II)-IDA at different pH conditions.*

[Ni(II)-IDA] (mmol/L)	Pseudo-first-order rate constant ($x10^{-2}$) (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	0.955	5.98	0.898	3.99	0.874	1150	0.993	117.3	0.953	49.04	0.919
0.5	27.41	0.852	7.13	0.905	4.37	0.938	1389	0.935	265.9	0.988	79.39	0.980
0.7	34.55	0.895	9.21	0.924	5.06	0.941	2273	0.914	311.2	0.991	101.3	0.986
1.0	55.73	0.912	18.42	0.964	11.28	0.987	2640	0.990	521.8	0.952	143.2	0.981
2.0	48.13	0.971	29.24	0.951	21.64	0.935	5991	0.866	1933	0.948	293.3	0.942
10.0	53.43	0.961	32.24	0.96	11.28	0.914	3829	0.939	1092	0.952	185	0.915

Using the k_1 values (obtained by pseudo-first-order rate constant values as well the pseudo-second-order rate constant), the overall rate constant 'k' was estimated. It was observed that the value of 'n' which was estimated for 1 and 2; best fitted for n=1; since the data was fairly fitted well to the pseudo-first-order rate constant values (*cf* figure 4.40). Therefore, using the pseudo-first-order rate constant values, the overall rate constant values along with the R^2 values were estimated at different pH values and returned in table 4-30. In general increasing the pH, the overall rate constant was decreased. The overall rate constant is found to be decreased from 538.0 to 105.0 L/mol/min as pH is increased from 8.0 to 10.0. Other group had studied the degradation of other complex compounds namely, weak-acid dissociable cyanides like $Cd(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$ with Fe(VI) at pH (9.1-10.5) (Yngard *et al.*, 2008). They reported that the rate laws for the oxidation of these compounds may be expressed as: $-d[Fe(VI)]/dt=k[Fe(VI)][M(CN)_4^{2-}]^n$ where n=0.5 and 1 for $Cd(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$, respectively, obtaining the m=1 which is similar to our findings.

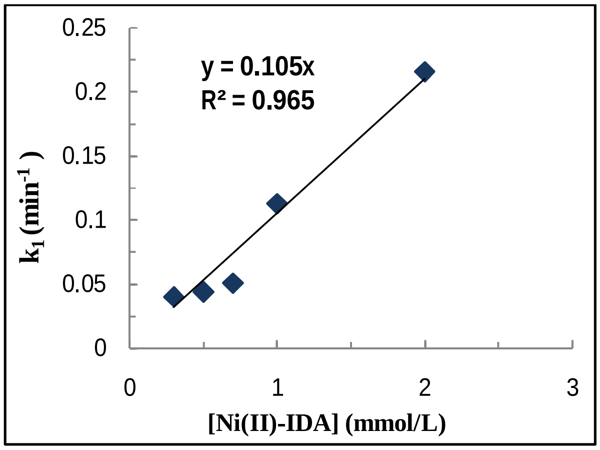


Figure 4.40. *Fitting of pseudo-first-order rate constant values with different concentrations of Ni(II)-IDA at pH 10.0.*

Table 4.30. *Overall rate constant in the decomplexation/degradation of Ni(II)-IDA by ferrate(VI) at different pH conditions*

pH	Ni(II)-IDA System	
	k (L/mol/min)	R^2
8.0	538	0.968
9.0	152	0.958
10.0	105	0.965

4.2.9.2. Mineralization of IDA

The treated samples were further subjected to TOC analysis to observe the degradation/mineralization of IDA following the decomplexation of Ni(II)-IDA complexes by Fe(VI). The total organic carbon data obtained for the varied stoichiometric ratios of Fe(VI) and Ni(II)-IDA (1:03 to 1:10) treated at various pH conditions i.e., pH 8.0 to 12.0 were shown in Table 4.31 in terms of percent change in TOC. Also the same data was represented graphically in Figure 4.41. From the data, it was observed that organic IDA species was effectively degraded/mineralized by Fe(VI). In fact, IDA was found to be completely mineralized for most of the varied concentration of Ni(II)-IDA, i.e., upto 1:1 stoichiometric ratio of Fe(VI) and Ni(II)-IDA. However, at higher concentrations of Ni(II)-IDA, i.e., 2.0 and 10.0 mmol/L, the degradation of IDA was lowered significantly for all the varied pH conditions. Hence, the degradation of organic species of IDA from Ni(II)-IDA complexes by Fe(VI) was favored at lower pH conditions. Increasing the pH from 8.0 to 12.0, the corresponding decrease in TOC removal percent was found to be from 26.11% to 19.17%, respectively at the same dose of Fe(VI) i.e., 1.0 mmol/L and the concentration of Ni(II)-IDA 10.0 mmol/L. Other organic compounds such as naphthalene and trichloroethylene were also reported to be completely mineralized in presence of Fe(VI) (DeLuca *et al.,* 1983)

Table 4.31. *Removal of IDA from Ni(II)-IDA complex species by Fe(VI) at different pH values*

pH	**% Removal of IDA by using Ferrate(VI)**					
	Fe(VI) : [Ni(II)-IDA]					
	01:0.3	**1:0.5**	**1:0.7**	**1:1**	**1:2**	**1:10**
8	100.00	100.00	100.00	100.00	39.25	26.11
9	100.00	100.00	100.00	100.00	36.09	24.77
10	100.00	100.00	100.00	100.00	23.12	19.17

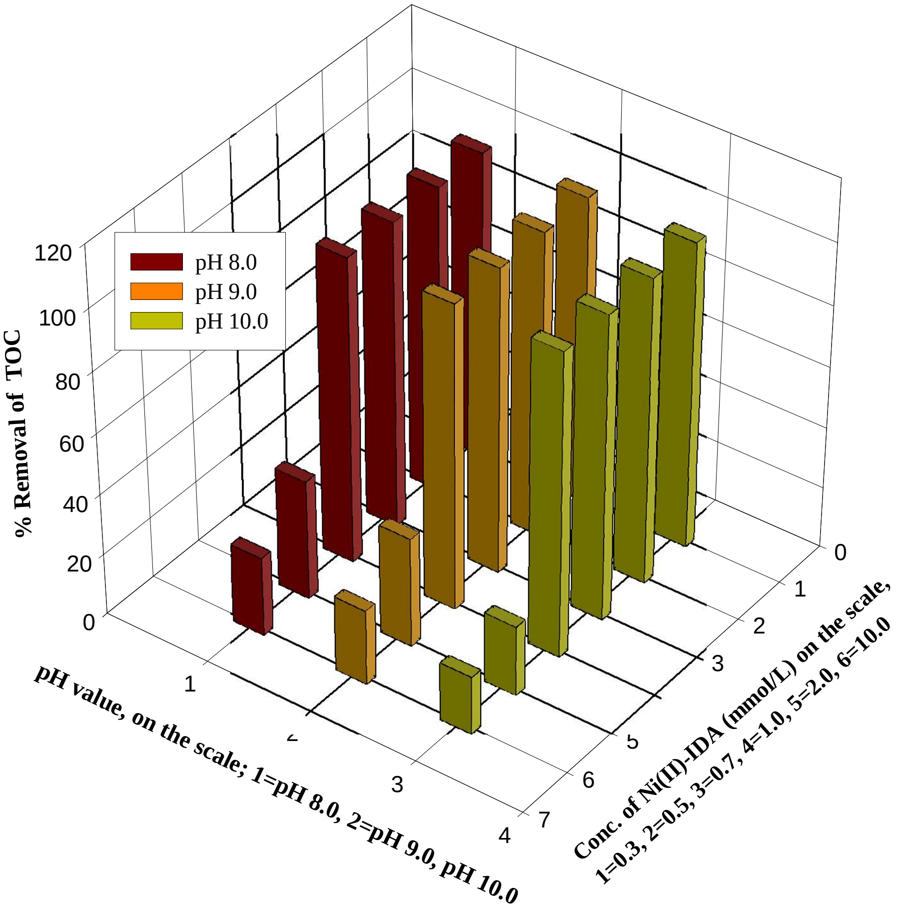


Figure 4.41. *Degradation of IDA for different concentrations of Ni(II)-IDA treated with Fe(VI):1.0 mmol/L at different pH values.*

4.2.9.3. Simultaneous removal of Ni(II)

The study was further extended for the simultaneous removal of Ni(II) from the Fe(VI) treated samples by analyzing the treated and filtered samples at the treated pH as well at the higher pH i.e., pH 12.0 by raising the treated solution pH 12.0 adding drop wise conc. of NaOH solution. The percent removal of Ni(II) was tabulated in Table 4.32 and presented graphically in Figure 4.42. The data indicated very low percent removal of Ni(II) was occurred at lower pH values, especially for the higher concentrations of Ni(II)-IDA. However, when the treated sample pH was raised to 12.0, a relatively higher percent removal of Ni(II) was obtained for the varied molar concentrations of Ni(II)-IDA. These results again indicated that the free Ni(II) ions from the decomplexed Ni(II)-IDA species were coagulated markedly at higher pH values by Fe(VI).

Table 4.32. *Percent removal of Ni(II) from various concentrations of Ni(II)-IDA complexed systems by Fe(VI) at different pH values.*

Fe(VI) : Ni(II)-IDA	**% Removal of Nickel by Fe(VI)**					
	pH 8.0	**Raised to pH 12.0**	**pH 9.0**	**Raised to pH 12.0**	**pH 10.0**	**Raised to pH 12.0**
1:0.3	21.05	85.50	23.33	82.20	20.69	83.33
1:0.5	8.06	45.00	3.45	50.00	5.17	37.04
1:0.7	2.63	35.00	2.70	25.00	1.37	21.74
1:1	0.94	32.00	0.00	18.50	0.00	9.68
1:2	0.00	10.00	0.00	6.00	0.00	2.78
1:10	0.00	0.00	0.00	2.00	80.00	1.41

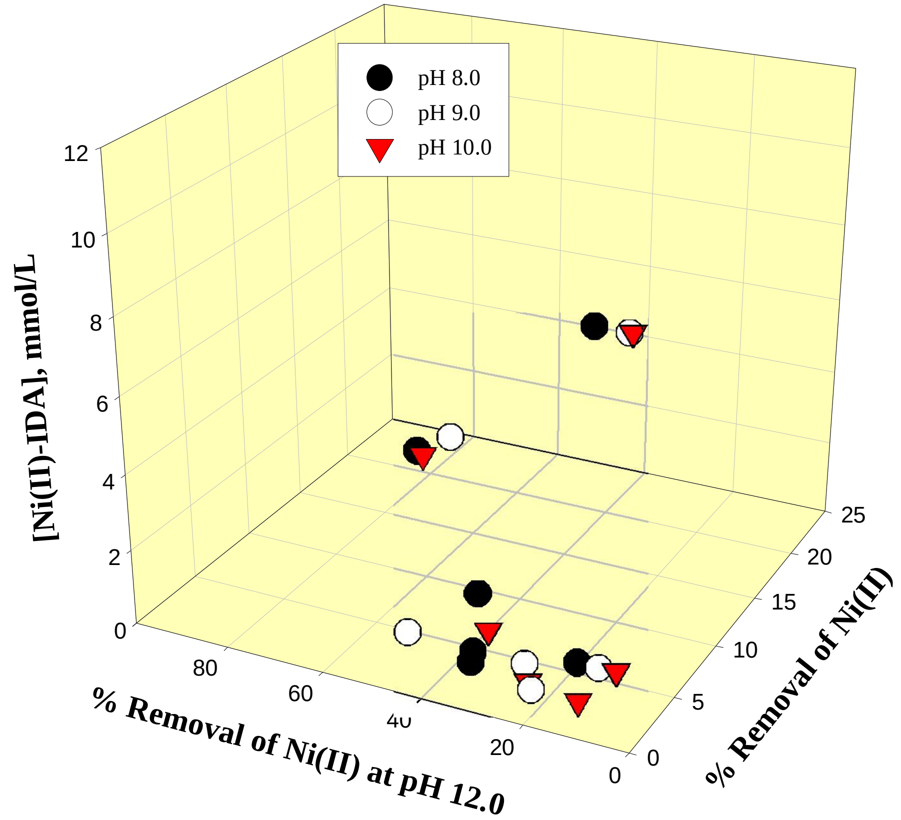


Figure 4.42. *Simultaneous removal of Ni(II) for different concentrations of Ni(II)-IDA treated withFe(VI): 1.0 mmol/L at different pH value*

4.2.10. Discussion of the M(II)- Complexed Systems

The present investigation studies various metal complexed systems *viz.*, M(II)-IDA; M(II)-NTA and M(II)-EDTA where M(II) stands for Cu(II), Cd(II), Zn(II) and Ni(II). These metals complexed species were treated with the Fe(VI) doses under the batch reactor operations. The studies were conducted with the various molar ratios of contaminant species with Fe(VI) i.e., from 0.3:1 to 15:1. The treatment data were collected with three different analytical ways *viz.*, the UV-Vis absorbance data, TOC and AAS data. The UV-Vis data was enabled to estimate the change in Fe(VI) concentration in presence of contaminants. Moreover, the change in Fe(VI) concentration with time could provide to deduce the kinetics involved in the oxidation process. Also it could help in discussing the mechanism involved with the oxidation of complexed species by Fe(VI). Moreover, the TOC data collected could enable to show the mineralization of organic component from the treated water. Further, the treated samples were filtered and analyzed for the total bulk metal concentration which enabled studying the coagulation/flocculation removal of free metals from aqueous wastes.

The time dependence data as obtained by the UV-Vis spectrophotometer, indicated that the removal of Fe(VI) was fitted to the pseudo-first and pseudo-second order rate equations to each of the concentrations of the reactants. A reasonably good fitting of the data was obtained for these systems studied for both the rate kinetics. Further, the first and second order rate constants values were further incorporated in the evaluation of the overall rate constants and it was observed that the pseudo-first order rate constants were best fitted for all the studied concentrations of the M(II)-organics; therefore the overall rate constants were evaluated with the degradation stoichiometry suggested as 1:1 for each reactants. The relative pseudo-first order rate constants were followed with the order Ni(II)-IDA> Cd(II)-IDA> Zn(II)-IDA Cu(II)-IDA> Cd(II)-EDTA> Cu(II)-NTA> Cu(II)-EDTA.Similarly, the overall rate constants also followed the similar trend. These results were in correlation with the stability of the given complexed species in solution as compiled elsewhere (www.dojindo.com). The stability constants values reported for these metal cations were found maximum with EDTA followed by the NTA and IDA complexes (Table 4.33). The other studies indicated that Cu(II) complexed species with the organic ligands *viz.*, EDDA, IDA, NTA and EDTA as treated with the Fe(VI). The rate of decomposition of Fe(VI) followed the order of Cu(II)-EDDA>Cu(II)-IDA>Cu(II)-NTA~Cu(II)-EDTA which is in accordance to the stability constants of these complexes in solutions (Yu *et al.*, 2010). The second order rate constants obtained in the degradation of IDA, NTA and EDTA (pure samples) by Fe(VI) was found to be $3.8x10^{2-}$, $4.4x10^{2-}$ and $8.6x10^{2-}$, respectively for IDA, NTA and EDTA (Noorhasan *et al.*, 2007). These results, although obtained for the pure organic compounds, again followed the same order as obtained with the present investigation. The studies conducted in the degradation of Zn(II)-cyanide complexed species with Fe(VI) showed that the oxidation rate of Zn(II)-cyanide with Fe(VI) was first-order and half-order with respect of the Fe(VI) and Zn(II)-cyanide, respectively. Moreover, the degradation was favored with increasing the pH and it was primarily related to the reactivity of $Zn(II)(CN)_4^{2-}$ with the $HFeO_4^-$ species (Yngard *et al.*, 2007).

The increase in pH caused to decrease in rate of Fe(VI) removal (i.e., pseudo-first order or pseudo-second order rate constants) at all studied molar ratios of M(II)-ligand species. Further, the overall rate constant was also decreased with an increase in pH from pH 8.0 to 12.0. This could be explained with the fact that the Fe(VI) is more reactive at lower pH values since the redox potential of ferrate(VI) at pH 1.0 is 2.20 V whereas it is 0.72 V at pH 14.0. This clearly showed that decreasing the pH, the spontaneous degradation of Fe(VI) was increased or the reactivity was increased, significantly (Tiwari *et al.*, 2005; Sharma, 2002, and Jiang and Lloyd, 2002). In other words the hydrated species of ferrate(VI) are more reactive than fully deprotonated species of Fe(VI). The speciation species of ferrate(VI) showed that at pH 8.0 an enhanced level of $HFeO_4^{-}$ species were dominant whereas at pH 10.0 or beyond that, the deprotonated species FeO_4^{2-} was the only species present in solution. Various acid-base-dependent Fe(VI) species may be expressed as:

$H_2FeO_4 \leftrightarrow HFeO_4^{-} + H^{+}$; $pK_a^1 = 3.50$ (Rush *et al.*, 1996)

$HFeO_4^{-} \leftrightarrow FeO_4^{2-} + H^{+}$; $pK_a^2 = 7.23$ (Sharma *et al.*, 2001)

The hydrated species of ferrate(VI) is highly reactive and reported that various stable inorganic and organic pollutants in water could be degraded efficiently (Sharma, 2002; Lee Y. *et al*., 2004; Tiwari *et al*., 2005). 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 thiocynate were evaluated (Sharma *et al.*, 2002). Further, the plot between k_1 versus SCN^{-} concentrations was found to be linear, hence, suggested that the rate law for this reaction was first order with respect to 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 (Sharma *et al.*, 2008b). It was reported that the protonated species were increased with decrease in solution pH and hence; increased the reactivity with the acidity since the spontaneous decomposition of Fe(VI) was more at lower pH values (Carr *et al.*, 1985). Moreover, the partial radical character ($Fe^{VI} = O \leftrightarrow Fe^{V}\text{-}O^{\bullet -}$) of ferrate(VI) was also in consistent to stabilize the proton and therefore increased the reactivity with cyanides. It was also reported that the protonated $HFe^{VI}O_4^{-}$ species possessed with larger spin density than the deprotonated species $Fe^{VI}O_4^{2-}$, which caused to increase the reactivity of Fe(VI) (Li *et al*., 2008; Sharma *et al*., 2004; Ohta *et al.*, 2001).

Additionally, increasing the M(II)-IDA, M(II)-NTA or M(II)-EDTA concentrations with a constant dose of Fe(VI) at a particular pH, in general, was caused to increase the pseudo-first order or pseudo-second order rate constant values. Previously, it was reported that an increased in pollutant concentration caused to increase the degradation rate of Fe(VI) however, the percent removal of TOC was reported to be less and enhanced level of intermediates were formed (Li *et al*., 2008; Lee *et al*., 2008).

Table 4.33. *Stability constant values for the metal(II) complexes*

Sl. No.	Metal	EDTA	NTA	IDA
1.	Cu(II)	18.80	12.96	10.63
2.	Ni(II)	18.62	11.54	8.90
3.	Zn(II)	16.50	10.66	7.27
4.	Cd(II)	16.46	9.54	5.73

On the other hand, the TOC data obtained for these systems showed that decreasing the pH of the solution was caused to increase the percent TOC removal i.e., it favored in mineralization of the organic compound significantly. This is in a line to the UV-Vis data obtained since enhanced rate of decomposition of Fe(VI) occurred at lower pH values. This suggested again that the Fe(VI) was more reactive at lower pH than at higher pH values. Moreover, increasing the ratios of M(II)-ligand with Fe(VI) caused a significant decrease in percent TOC removal or in other words, decreasing the Fe(VI) to M(II)-ligand ratios caused to decrease the TOC removal. This is obvious with the fact that decreasing the oxidizing dose i.e., Fe (VI) rendered to decrease in percent TOC removal. This is in a line with previous studies; enabled that increasing the Fe(VI) dose (ferrate(VI):BPA ratio) the value of DOC was 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 was found greater than 1, indicating that some intermediates of BPA was formed but with the time, the intermediates were also degraded/oxidized and mineralized (Li et al., 2008).

Further, the simultaneous removal of metal(II) ions, perhaps, by the coagulation and flocculation process was enhanced with the increase in pH. It was interesting to note that the removal of metal(II) was decreased increasing the pH of the solutions i.e., pH from 11.0 to 8.0 significantly. However, increasing the treated sample pH to 12.0 was caused a significant increase in percent removal of these metals and at cases like Cu(II), Cd(II) and Zn(II) the removal of metal(II) was more than 90% at all studied ratios of M(II)-ligand:Fe(VI). Previously, it was observed that at higher ratios of the M(II)-ligand: Fe(VI), a significant decrease in TOC was observed; these results, therefore indicated that Fe(VI), even at higher concentrations of M(II)-ligand caused to decomplex these complexed species. The free metals were hence, coagulated/flocculated significantly at higher pH values. The previous reports also indicated that the ferric(III) oxide, produced from the treatment, acted as a coagulant in the removal of several metals, non-metals and even radionuclides (Waite and Gray, 1984; Jiang and Lloyd, 2002; Potts and Churchwell, 1994). Moreover, increasing the solution pH enhanced remarkably the coagulation/precipitation of free metals ions in aqueous solutions which, perhaps, enhanced the percent removal of metal(II) ions by increasing the solution pH (Larson and Pugh, 1998). Other studies also indicated that a significant percent of Cu(II) or Ni(II) was removed simultaneously as treated by Fe(VI) at different pH values (Lee and Tiwari, 2009). Moreover, the Cu(I)-cyanide was treated with Fe(VI) and with increasing the dose of Fe(VI) enabled to remove completely the Cu(II) simultaneously by reduced Fe(III) (Sharma *et al*., 2005a). Relatively, the Ni(II) was removed with lesser percent level comparing to other metal(II) ions (i.e., Cu(II), Cd(II) and Zn(II)), this could be explained with the fact that the coagulation of nickel was less comparing to other metal(II) ions. The similar observations were also reported previously when the Ni(II)-cyanide complexed species were treated with Fe(VI) (Lee and Tiwari, 2009).

4.3. IC Measurements for the study of degradation of Metal(II)-organic complexes by Ferrate(VI)

4.3.1. pH dependence study

The decomplexation ofmetal complexed systems due to Fe(VI) treatment was directly measured with the help of IC analysis. Cu(II)-EDTA system was used to study the effect of pH on the decomplexation of the complex in presence of Fe(VI). The study was carried out by treating 0.10 mmol/L of Cu(II)-EDTA with 2.4 mmol/L of Fe(VI) for 60 minutes at different pH conditions. Keeping the ionic strength in the solution fixed as 0.01 M with $NaNO_3$. The pH of the solution was maintained within ±0.1 of the desired value using the 0.01 M NaOH or 0.01 M HNO_3 during the reaction period. Aliquots of the solution were periodically removed from reactors and rapidly filtered through 0.45 μm membrane filters and subjected to ion chromatograph (Metrohm Modular IC System), previously calibrated with the known concentrations of Cu(II)-EDTA at the same pH in order to observe the change in concentration of Cu(II)-EDTA with time at that pH value. The IC results were obtained as a function of time and at different pH. From the results obtained, the percent decomposition of Cu(II)-EDTA for different pH value was represented in Figure 4.43. It was observed that the acidic condition favored the decomplexation of Cu(II)-EDTA; while the decomplexation maintained almost 100% up to pH 6.5, it was only *Ca* 35% at pH 9.9. This suggestedthat the decomlexation process was highly acid catalyzed. Moreover, it was also reported and observed that the protonated species of Fe(VI) i.e., $HFeO^{4-}$ and H_2FeO_4 were comparatively more reactive than the deprotonated species FeO_4^{2-}. Yang and Davis also reported favorable decomplexation of Cu(II)-EDTA at lower pH from photocatalytic oxidation (PCO) with illuminated TiO_2. (Yang and Davis, 2000a). As EDTA had two types of ligating groups such as amine and carboxyl, they reported that PCO reactions were initiated at either a carboxyl or amine group, depending on pH. At lower pH, the PCO reaction proceeded favorably via radical formation at a carboxyl group complexed to the TiO_2 surface (Yang and Davis 2000b). Lockhart and Blakeley reported the formation of EDTA (ethylenediaminetriacetic acid) during aerobic photodegradation of Fe(III)-EDTA (Lockhart and Blakely, 1975).Various protonated and deprotonated species of ferrate(VI) were present in solution and these species were prevalent at different solution pH which clearly indicated that $HFeO_4^-$ and FeO_4^{2-} were predominant in neutral and alkaline pH, in which Fe(VI) was known to be relatively stable towards its spontaneous decomposition to ferric ion (Fe(III). The figure also indicated that at pH~10 the only species i.e., FeO_4^{2-} existed in aqueous solutions. As Cu(II)-EDTA is a strong chelating complex, most species of Cu(II) complexed with EDTA in the studied pH range. Otherwise, two forms of Fe(VI), namely,$HFeO_4^-$ (85%) and H_2FeO_4 (15%)can react with Cu(II)-EDTA at pH 4.0. However, at pH 10.0, as most ferrateis present as $HFeO_4^-$, a single species of Fe(VI) reacted with Cu(II)-EDTA. The rapid decomplexation of Cu(II)-EDTA at pH 4.0 compared to pH 10.0 was probably resulted from different speciation of Fe(VI). $HFeO_4^-$ and H_2FeO_4, which were regarded as relatively more reactive species than the unprotonated speciesFeO_4^{2-}, were predominant species below neutral pH. Also the redox potential of ferrate(VI) was comparatively very high in acidic medium as compared to the alkaline medium which can be seen from the reduction potentials of Fe(VI) in acidic and alkaline solutions, i.e.,+ 2.20 V and + 0.72 V respectively. Therefore a powerful oxidizing condition was provided at the elevated concentration of the Fe(VI) species such as $H_3FeO_4^+$ and H_2FeO_4.

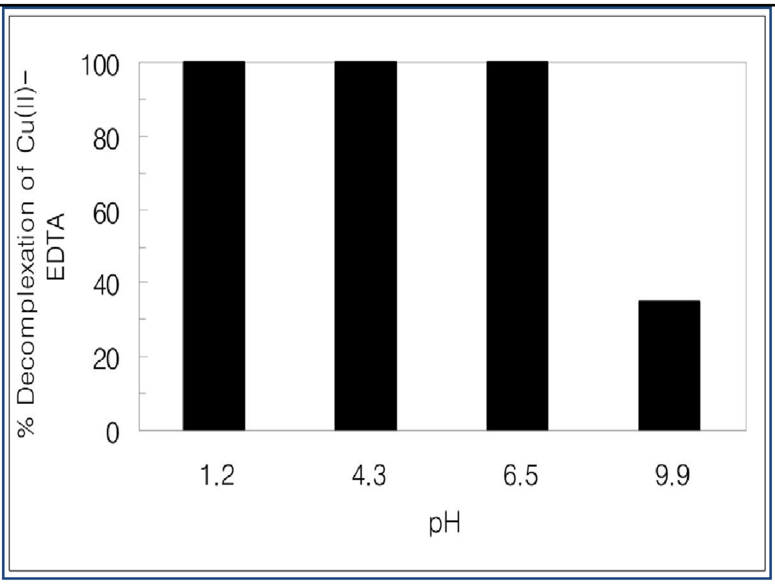


Figure 4.43. *Decomplexation of Cu(II)-EDTA at various pH values (Initial [Cu(II)-EDTA]: 0.10 mmol/L; Fe(VI) dose: 2.4 mmol/L)*

4.3.2. Time dependence study/ Kinetics of the decomplexation of Cu(II)-EDTA

Time dependence and the kinetics of the decomplexation of Cu(II)-EDTA was observed at two different pH (i.e., 4.0 and 10.0). The initial Cu(II)-EDTA concentration was kept constant at 0.10 mmol/L, and the ferrate(VI) dose was taken 2.40 mmol/L. Results obtained were shown in Figure 4.44. It was noted that at lower pH (i.e., pH 4.0) the decomplexation reaction was extremely fast, and 100% of Cu(II)-EDTA was decomplexed within 5 to10 min of contact. However, at higher pH (i.e., pH 10.0) the decomplexation process was relatively slow and it was observed that even after 180 min of contact, maximum *Ca* 37% of Cu(II)-EDTA was decomplexed. As TiO_2-mediated photocatalytic treatment was widely used to deal with wastes containing EDTA complexed metals ions, the percentage disappearance of Cu(II)-EDTA by ferrate (VI) was comparable with that by TiO_2-mediated photocatalysis (Yang and Davis 2000a).Yang and Davis reported that the aqueous initial decomplexation rate (r_{aq}) of Cu(II)-EDTA at pH 4, developed from the linear portion of all aqueous Cu(II)-EDTA concentrations with respect to time from 0 to 10 min, was 3.0×10^{-6} mol/ L/min(Yang and Davis 2000a). However, the aqueous initial decomplexation rate (r_{aq}) of Cu(II)-EDTA by ferrate(VI) at pH 4.0 was 7.5×10^{-6} mol/L/min, suggesting ferrate(VI) was more efficient oxidant than TiO_2-mediated photocatalytic reaction in the decomplexation of Cu(II)-EDTA at acidic condition.

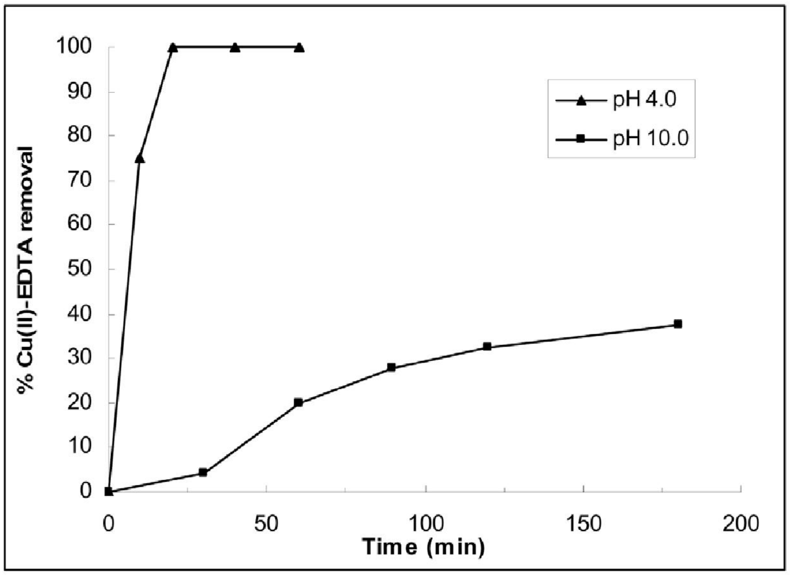


Figure 4.44. *Removal percent of Cu(II)-EDTA as a function of time at different pH values (Initial [Cu(II)-EDTA]: 0.10 mmol/L; Fe(VI) dose: 2.4 mmol/L]*

Since the decomplexation of Cu(II)- EDTA was seemingly very fast at lower pH, the data obtained at higher pH was used to discuss the kinetics of the decomplexation. Further, in order to obtain a quantitative information for the decomplexation of Cu(II)-EDTA in aqueous phase, the following simple irreversible reaction, expressed as equations (4.43) and (4.44) below, was assumed to occur.

$$\text{Fe(VI)} + \text{Cu(II)-EDTA} \rightarrow \text{Fe(III)} + \text{Products} \quad \ldots(4.43)$$

$$-\frac{d[\text{Cu(II)-EDTA}]}{dt} = k\,[\text{Fe(VI)}]^m\,[\text{Cu(II)-EDTA}]^n \quad \ldots(4.44)$$

where k represents the overall rate constant of the reaction (4.43) and the [Fe(VI)] and [Cu(II)-EDTA] are the molar concentrations of Fe(VI) and Cu(II)-EDTA, respectively, m and n are the orders of the reaction with respect to each reactant. Since, the concentration of Fe(VI) was 24 times higher than that of Cu(II)-EDTA, under pseudo-first-order condition, we may write the equation (4.44) as:

$$-\frac{d[Cu(II)\text{-}EDTA]}{dt} = k\,[\mathrm{Cu(II)\text{-}EDTA}]^n \qquad \ldots 4.45$$

The change in concentration of Cu(II)-EDTA was analyzed as a function of time and tried to simulate the data for first and second order reaction equations (Figures 4.45(a) and 4.45(b)), but observed values were slightly fitted well with the second-order-rate equation (correlation coefficient: 0.952) than the first order rate equation (correlation coefficient: 0.925).

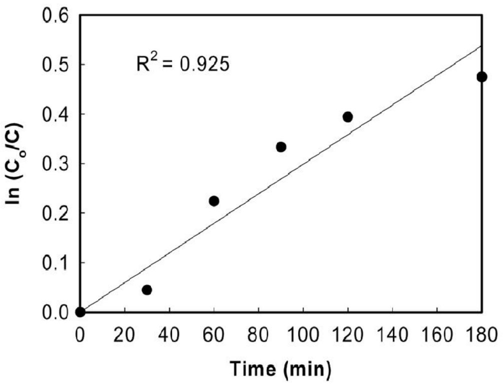


Figure 4.45(a). *First order rate kinetics [ln (C_o/C) vs time]*

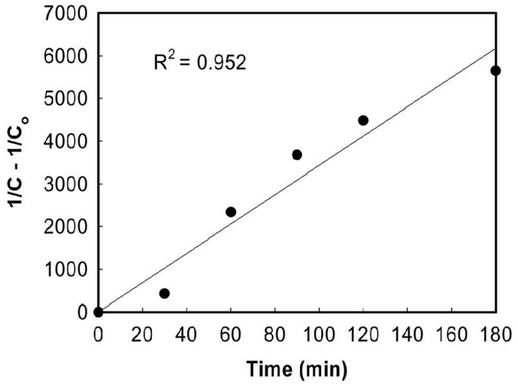


Figure 4.45(b): *Second order rate kinetics [1/C-1/C_o vs time]*

4.3.3. Simultaneous Removal of Cu(II)

The simultaneous Cu(II) removal was also observed at the two pH values i.e., 4.0 and 10.0. It was assumed that with the reduction of Fe(VI) into Fe(III), it may help to adsorb/coagulate the free Cu(II) ions in solution. The solution was filtered with 0.45 µm syringe filter, and the Cu(II) content was analyzed using AAS. The results obtained were shown in Figure 4.46. Again, the removal of free Cu(II) ions was rapid at lower pH (i.e., pH 4.0) whereas, it was slow at higher pH (i.e., 10.0). Moreover, maximum *Ca* 52% of Cu(II) was removed from the solution at either of the pH i.e., pH 4.0 or 10.0. Decomplexation of 100% at lower pH, but slow removal of free Cu(II) was explicable due to the reason that at lower pH values the adsorption/coagulation capacity of Fe(III) was greatly retarded (Larson and Pugh, 1998). On the other hand, at higher pH values the decomplexation of Cu(II)-EDTA was partial, hence, lower Cu(II) removal occurred. Further, it was observed that the column of IC was greatly contaminated with the coagulated small sized Fe(III) particles and making great hindrance performing the column operations hence, the other systems were refrained to be performed herewith.

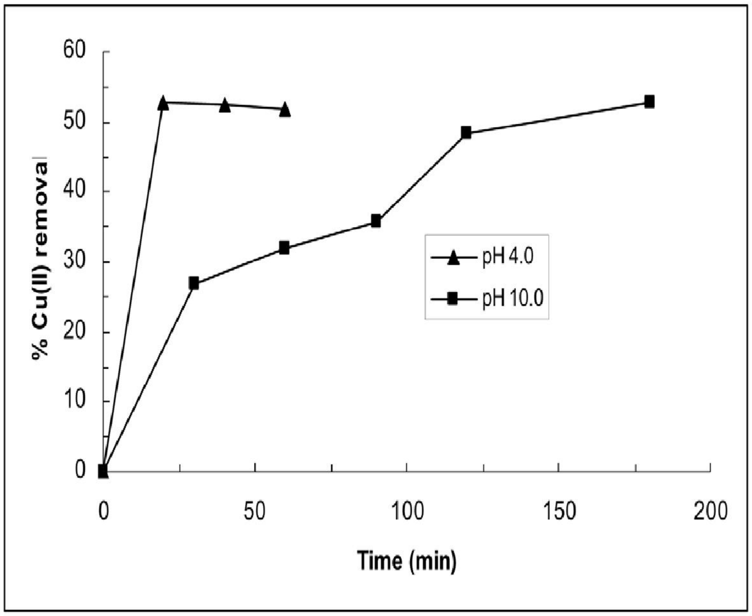


Figure 4.46. *Percent removal of Cu(II) as a function of time at different pH values (Initial [Cu(II)-EDTA]: 0.10 mmol/L; Fe(VI) dose: 2.4mmol/L)*

4.4. Effect of ionic strengths and types of background electrolytes on the decomplexation of Metal complexes by Fe(VI)

The Zn(II)-NTA complexed system was taken to study the effect of ionic strength and back ground electrolytes on the decomplexation efficiency of Fe(VI). Zn(II)-NTA solution (1.0 $x10^{-4}$ mol/L 1.0$x10^{-2}$ mol/L) was taken in a reactor and the pH was adjusted to an specified value by addition of drops of conc. HNO_3/NaOH solutions, a known amount of Fe(VI) was introduced into it under the stirring condition. At a constant time interval, a portion of sample was removed from the reactor and then a concentrated quenching solution (2.0 mol/L Na_2SO_3) was added into the each sample. The change in concentration of ferrate as a function of time was checked with the help of UV-visible spectrophotometer (UV-1601, Shimadzu). Similarly, the change in total zinc concentration was checked after filtration of Fe(VI) treated samples using 0.45 μm syringe filter and was analyzed by an inductively coupled plasma (Optima 2000 DV, Perkin-Elmer). The degradation of NTA was measured by TOC (total organic carbon) analyzer (Shimadzu 5000). The pH measurement was done using Orion pH meter unit 720A, USA.

4.4.1. Effect of Ionic Strength

Figure 4.47 showed the reduction efficiency of Fe(VI) at different ionic strengths with $NaNO_3$ concentration ranging from 1.0 mmol/L to 1.0 mol/L at pH 9.2 as a function of time.Fe(VI) reductionwas gradually increased as reaction time increased and approximately 50% of the initial Fe(VI) was reduced after 180 mins. Moreover, it was observed that even for 1000 times increase in ionic strength ($NaNO_3$), the reduction of Fe(VI) was almost unaffected upto 180 mins of contact. This result suggested that $NaNO_3$ was unable to effect the redox reaction of Zn(II)-NTA by Fe(VI).

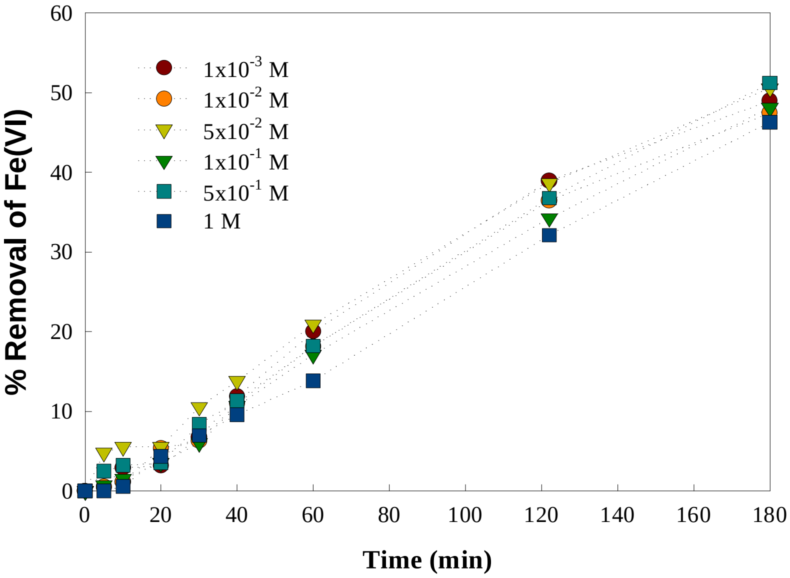


Figure 4.47. *Reduction of 0.10 mmol/L Fe(VI) as a function of time at different ionic strength with* $NaNO_3$ *([Zn(II)-NTA] = 1.0mmol/L).*

4.4.2. Effect of background electrolytes

Further, Figure 4.48 showed the reduction efficiency of Fe(VI) at seven different types of background electrolytes at the same concentration as a function of time. With the exceptions of $NaNO_2$ and Na_2SO_3, reduction efficiency of Fe(VI) was similar for all other employed background electrolytes over the entire reaction time. This result can suggest that completely oxidized anions such as ClO_4^-, NO_3^-, SO_4^{2-}, PO_4^{3-} as well as redox insensitive anions such as $Cl^-$was not participated in the reduction of Fe(VI).Therefore Fe(VI) reduction was not affected by the concentration of completely oxidized background electrolytes. Meanwhile, more rapid Fe(VI) reduction was observed in the presence of SO_3^{2-} rather than NO_2^-. The greater Fe(VI) reduction by the Na_2SO_3 and $NaNO_2$ compared to other five background electrolytes was explained by the favorable oxidation of SO_3^{2-} and NO_2^- those were meta-stable in oxidation state to completely oxidized SO_4^{2-} and NO_3^- states, respectively. It was reported that Fe(VI) rapidly oxidized sulphur intermediates such as $S_2O_3^{2-}$ and SO_3^{2-} with faster rate ($t_{1/2} < 7$ s) yielding sulphate (Sharma, 2002). Goff and Murman used ^{18}O-enriched-ferrate tracer in studying oxidation of sulphite (SO_3^{2-}) by Fe(VI) to demonstrate that the oxygen is transferred from Fe(VI) to form sulphate (SO_4^{2-}), a final reaction product (Goff and Murman, 1971). The rate constant for sulphide oxidation by Fe(VI) was $1.8x10^3$ $M^{-1}s^{-1}$ at pH 9.9 (Johnson and Read, 1996). The rate constant for nitrite oxidation by Fe(VI) at 25°C was $5.8x10^{-2}M^{-1}s^{-1}$ at pH 9.9 (Sharma *et al.*,1998a). Similarly, the reduction of oxyiron(V) by sulphite and thiosulfate in aqueous solution was studied using premix pulse radiolysis technique (Sharma and Cabelli, 2009). Moreover, the reactions of $Fe^{VI}O_4^{2-}$ with two sulphur radicals were also studied. The rate constants for the reduction of $Fe^{VI}O_4^{2-}$ to $Fe^{v}O_4^{2-}$ by sulphite and thiosulfate radicals were reported to be $(1.9±0.3)x10^8$ and $(7.5±0.3)x10^7$ $M^{-1}s^{-1}$, respectively. These observations suggested that a competitive reduction might occur between Zn(II)-NTA and Na_2SO_3 or $NaNO_2$ in the reaction with Fe(VI). In these competitive conditions, Fe(VI) could more favorably react with Na_2SO_3 / $NaNO_2$ rather than Zn(II)-NTA.

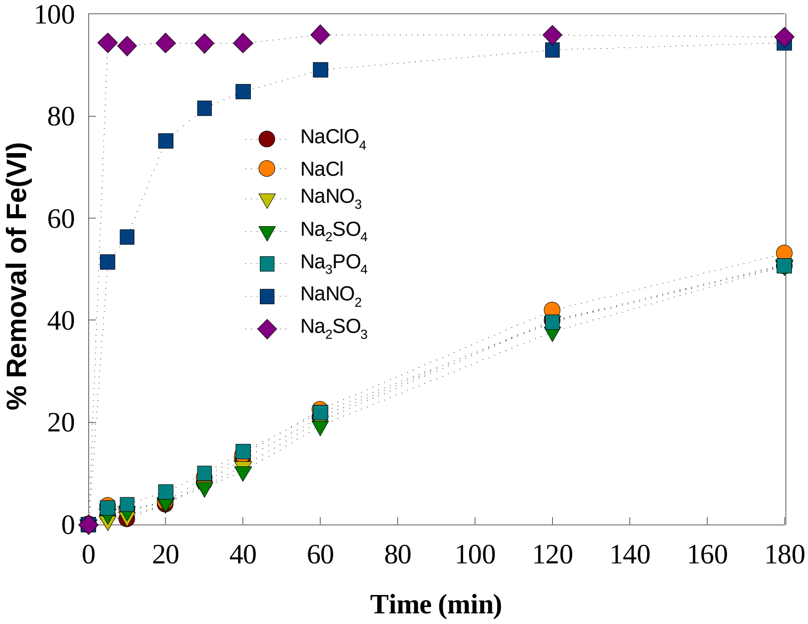


Figure 4.48. *Reduction of 0.1 mmol/L Fe(VI) as a function of time at seven different background electrolytes ([Zn(II)-NTA] = 1.0mmol/L)*

4.4.3. Variation of TOC in presence of background electrolytes

The variation of total organic carbon (TOC) concentration as a function of time at different type of background electrolytes was shown in Figure 4.49. The removal of TOC in presence of completely oxidized anions such as NO_3^- and PO_4^{3-} was between 40% and 60% after 3 hrs. In contrast, quite lower removal of TOC was observed in the presence of SO_3^{2-} and NO_2^- again supported the previous observation obtained by the UV-Visible measurements in the reduction of Fe(VI).

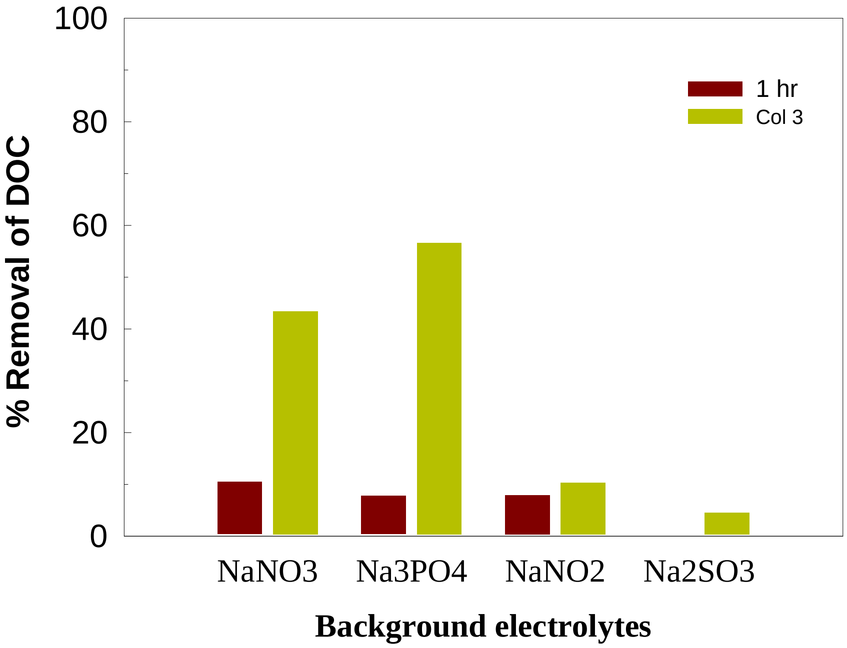


Figure 4.49. *Variation of the total organic carbon at different background electrolytes ([Fe(VI)] = 0.1 mmol/L, [Zn(II)-NTA] = 1.0 mmol/L)*

4.4.4. Effect of partially oxidized electrolytes (SO_3^{2-} and NO_2^-)

In order to further identify effects of the SO_3^{2-} and NO_2^- on the decomplexation of Zn(II)-NTA by Fe(VI), the Fe(VI) concentration was measured as a function of time at different concentration of the SO_3^{2-} and NO_2^-. As shown in Figure 4.50, decreasing the concentration of both SO_3^{2-} and NO_2^- caused to decrease the Fe(VI) reduction. This showed an interference effect of these two anions in the reduction of Fe(VI) by Zn(II)-NTA.

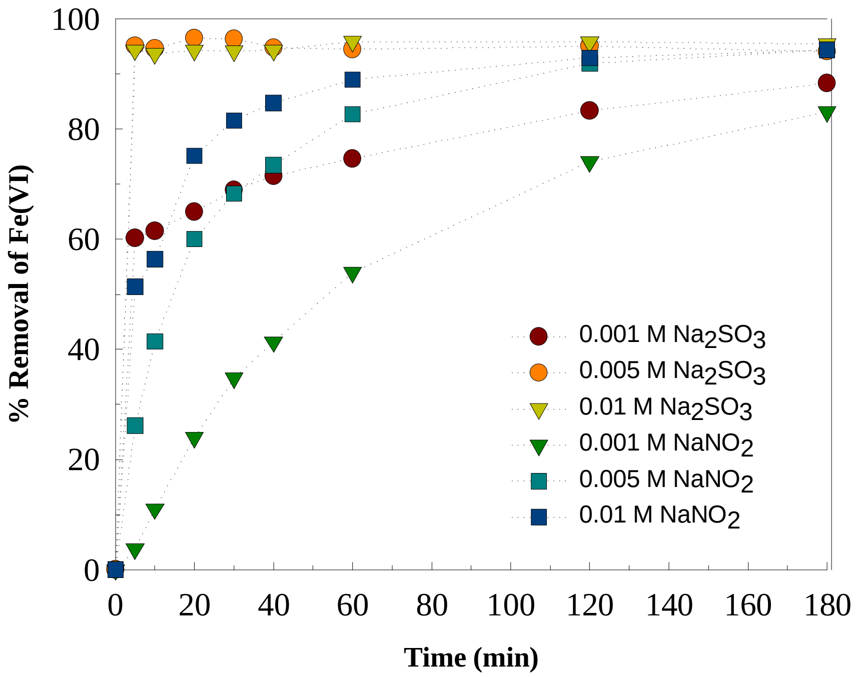


Figure 4.50. *Reduction of 0.1 mmol/L Fe(VI) as a function of time at seven different background electrolytes ([Zn(II)-NTA] = 1.0mmol/L)*

4.4.5. Removal of Zn(II) at different background electrolyte concentrations

Figure 4.51 showed the result of total Zn(II) removal after 1 and 3 hrs at different background electrolytes treated with Fe(VI) dose i.e., 0.1 mmol/L having Zn(II)-NTA 1.0mmol/L. For all background electrolytes, very similar removal of total Zn(II) was observed at two reaction times. This result clearly showed that the application of Fe(VI) was significantly minimized total soluble Zn(II) concentration. The reason for this removal of total soluble Zn(II) was explained by the precipitation/coagulation of Zn(II) species liberated from decomplexation of Zn(II)-NTA or by the adsorption of Zn(II) species onto Fe(III) which was formed from reduction of Fe(VI).

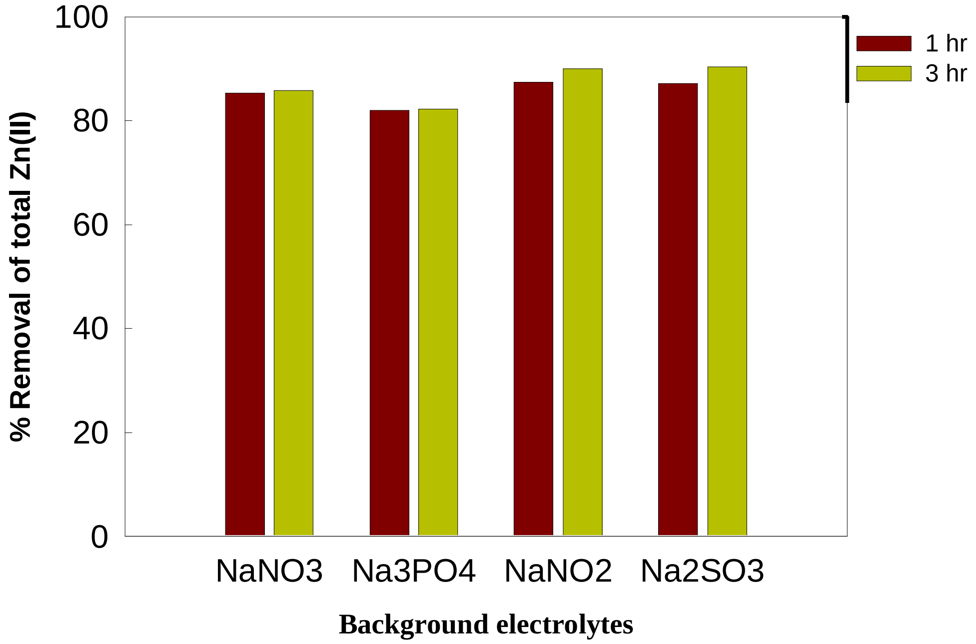


Figure 4.51. *Variation of total Zn(II) concentration after 1 and 3 hrs at different background electrolytes ([Fe(VI)] = 0.1 mmol/L, [Zn(II)-NTA] = 1.0mmol/L).*

CHAPTER 5

Conclusions

5. CONCLUSIONS

The higher oxidation state of iron, ferrate(VI) as potassium ferrate (K_2FeO_4) was synthesized in the laboratory by wet oxidation method as modified by Tiwari *et al*. (2007). The purity of the prepared ferrate(VI) was determined with the help of UV-Visible spectrophotometer at the wavelength of 510 nm and was found to be in excess of 95%. The highly reactive ferrate(VI) was fully employed to assess its efficiency/suitability in the degradation of organic pollutants *viz*., IDA, NTA and EDTA in their single form as well in the complexed forms (i.e., M(II)-IDA/or M(II)-NTA/or M(II)-EDTA) under the batch reactor operations. The batch experiments for the single systems of organic pollutants *viz.*, IDA, NTA and EDTA were conducted at solution pH 10.0. and as a function of concentrations of Fe(VI). The results infer that the reactivity of Fe(VI) is highly dependent on its concentration. It was observed from the UV-Visible analytical data that the increasing the dose of Fe(VI) enhances the degradation of these organic species with significant faster rate of decomposition. Just within *ca* 10-15 mins of contact time, Fe(VI) concentration attained a constant value indicating that most of the organic species are degraded (initial concentration was taken as 2.0×10^{-4} mol/L) within this period. The kinetic interpretations further confirm the higher reactivity of Fe(VI) at higher concentrations. The time dependence UV-Visible data obtained for these organic species were best fitted with the pseudo-first-order rate kinetics and from the rate constants obtained, it was quantitatively recorded that with increasing the dose of Fe(VI) from 0.5×10^{-4} to 7.0×10^{-4} mol/L, the rate of Fe(VI) degradation or indirectly the oxidation of the organic species was increased from 2.76×10^{-2} to 3.92×10^{-2} min^{-1}, 1.38×10^{-2} to 3.45×10^{-2} min^{-1} and 0.5×10^{-4} to 7.0×10^{-4} mol/L respectively for IDA, NTA and EDTA. The increased rate of degradation of the organic species under study with the increased dose of Fe(VI) is considered feasible with the fact that Fe(VI) is known to be less stable and hence more reactive at concentrated solution than in a dilute solution. It was further demonstrated by TOC nalysis that Fe(VI) is quite efficient in the degradation/mineralization of these organic species. Almost complete mineralization, *viz.*, 98.02 % removal of IDA was observed for the molar ratio of Fe(VI) and IDA as 1:03 at pH 8.0. whereas at pH 10.0, the percent removal of organic compound was recorded as 60.05%, 49.75% and 48.13% respectively for IDA, NTA and EDTA for the molar ratio of 1:0.5 for Fe(VI) and organic species. Ferrate(VI) possesses higher redox potential at acidic conditions and hence accounted for its enhanced reactivity to degrade the organic impurities at lower pH. Higher percent removal of organic species is observed at lower concentrations of the organic species for all the systems at constant dose of Fe(VI). Among these organic pollutants the degradation followed the order IDA>NTA>EDTA at pH 10.0 and at varied Fe(VI) dose.

Further, the study with the M(II) complexed IDA, NTA and EDTA is carried out extensively under the batch reactor operations where M(II) represented the important heavy metal toxic ions *viz.*, Cu(II), Ni(II), Zn(II), and Cd(II). Various parametric studies, *viz.*, effect of pH, concentration, time dependence kinetics, effect of ionic strength and type of background electrolytes were conducted in the treatment of such wastes by Fe(VI). The studies were performed with three different analytical ways as to deduce optimal conclusions of the present investigations. The UV-Visible based observations is obtained which could enable to observe the change in Fe(VI) concentration with time. The time dependence data was further utilized to deduce the kinetics of the reduction of Fe(VI), therefore the oxidation of organic pollutants. In some cases, the IC analysis was performed to observe directly the degradation /decomplexation of organic species in solution. The TOC analytical observations are taken to observe the mineralization of organic pollutants in solution with the Fe(VI) dose. Lastly, the removal of non-degradable impurities, *viz.*, the M(II) ions by the coagulation/flocculation process with the reduced Fe(III) is optimized by the AAS/ICP measurements. It was found that the reduced Fe(VI) into Fe(III) is an excellent coagulant/flocculent and hence could remove the free metal ions by sedimentation process or by simple filtration. The results obtained for each complex system indicate that the degree of the degradation/removal of metal complex species from aqueous solutions by Fe(VI) is greatly dependent on pH condition. The UV-Visible analytical data showed that significant degree of reduction of Fe(VI) occurred in presence of the pollutant species. This indicated that the Fe(VI) caused to decomplex/degrade the M(II)-organic species in solution. The reduction of Fe(VI) was favored at lower pH and was significantly retarded as pH was increased. The results are explicitly in conformity with the higher redox potential of Fe(VI) at lower pH values with significant increase in the stability at higher pH values; the redox potential of Fe(VI) is reported as 2.20 V at pH 1.0 whereas it is only 0.70 V at pH 12. Moreover, the protonated ferrate species i.e., $HFeO_4^-$ ($HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-}$; $pK_a^2=7.3$) is dominant at lower pH possessed with larger spin density than the deprotonated species *viz*., FeO_4^{2-} caused for increased reactivity of Fe(VI) at lower pH values. The time dependence data as obtained by the UV-Vis spectrophotometer indicated that the removal of Fe(VI) was fitted to the pseudo-first and pseudo-second order rate equations to each of the concentrations of the reactants. A reasonably good fitting of the data was obtained for these systems studied for both the rate kinetics. Further, the first and second order rate constants values were incorporated in the evaluation of the overall rate constants and it was found that the pseudo-first order rate constants were best fitted for all the studied concentrations of the M(II)-organics; therefore the overall rate constants were evaluated with the degradation stoichiometry suggested as 1:1 for each reactants. The relative pseudo-first order rate constants were followed with the order Ni(II)-IDA> Zn(II)-IDA> Cd(II)-IDA> Cu(II)-IDA> Cd(II)-EDTA> Cu(II)-NTA> Cu(II)EDTA. The overall rate constants also followed the similar trend. These results are in correlation with the stability of the given complexed species in solution as compiled elsewhere (www.dojindo.com). The complexes with higher stability constants showed relatively less value of overall rate constants. Further, the IC data is obtained for the system of Cu(II)-EDTA complex systems again indicates that lower pH favors the decomplexation of the complex as while the decomplexation attained almost 100% up to pH 6.5 whereas it was only *Ca* 35% at pH 9.9. Moreover, the concentration dependence studies shows that degradation of the complex species is generally enhanced with increasing concentration of the complex species at constant dose of Fe(VI). However, it is noted that at higher pH values(i.e., pH 11.0 or 12.0), the rate of decomposition of Fe(VI) was almost independent with increasing the concentration of complexes, apparently due to insignificant reactivity of Fe(VI) at higher pH value as suggested previously. The other complexed systems were not conducted further with IC measurements since the reduced ferrate(VI) i.e., Fe(III) flocs often block the IC columns.

The mineralization of the organic compounds in the M(II)-complexed species is conducted with the TOC measurements. The TOC data is collected at various stoichiometric ratio of the M(II)-complex as treated with Fe(VI) as a function of pH. The results indicated that the degradation/mineralization of organic pollutants was found to be effective with the Fe(VI) treatment. Decreasing the pH of the solution caused to increase in percent TOC removal i.e., it favored in mineralization of the organic compound significantly which was in a line to the UV-Vis data obtained separately since an enhanced rate of decomposition of Fe(VI) was occurred at lower pH values. Moreover, increasing the ratios of M(II)-ligand with Fe(VI) caused a significant decrease in percent TOC removal or in other words decreasing the Fe(VI) to M(II)-ligand ratios caused to decrease the TOC removal. It was interesting to note that a complete mineralization of organic species was attained for metal complexes having lower stability constant, *viz.*, Cd(II)-IDA and Ni(II)-IDA for lower concentrations of the metal complexes, *i.e.*, upto 1:1 ratio of Fe(VI) to metal complex at pH 8.0 to 10.0. For other metal complexed systems *viz.*, Cu(II)-IDA, Zn(II)-IDA, Cu-NTA, Cu(II)-EDTA and Cd(II)-

EDTA, partial degradation of the organic species occurred, with the percent removal ranged from 35.82% to 60.23% at pH 8.0. These results indicate that certain metal complexes, apparently with lower value of stability constant; the organic pollutants were decomplexed and mineralized completely. It was further reaffirmed, from the TOC data that lower pH favored the degradation of organic species, once again confirming the fact that Fe(VI) is less stable or more reactive at lower pH values.

The reduced ferrate(VI), i.e., Fe(III) is an excellent coagulant/flocculent. Therefore, simultaneous removal of the free metal ions from the degraded complex species was subsequently obtained by AAS data. It was observed that only partial or insignificant percent of metal ions are removed through coagulation/adsorption by Fe(III) at lower pH values. However, remarkably a sharp increase in percent removal of free metal ions is observed as the solution pH is elevated to higher pH values i.e., pH 12.0. It was observed that the removal of Cu(II), Cd(II) and Zn(II) from their complexed species was achieved to >90% at all studied ratios of M(II)-ligand:Fe(VI). A complete 100% removal of metal ions was observed in a number of treated samples at higher pH 12.0. The maximum percent removal of metal ions was recorded for Cd(II)-IDA system which also showed least value of stability constant among the systems studied. 100% removal of Cd(II) ions was occurred for the varied molar stoichiometric ratios of Fe(VI):Cd(II)-IDA, *i.e.,* from 1:0.3 to 1:2. It is evident from these results that the coagulation/flocculation capacity of Fe(III) is enhanced at higher pH values.

Further, the effect of ionic strength and background electrolytes on the decomplexation of the metal complex, *i.e.,* Zn(II)-NTA was assessed. The results have shown, the effect of ionic strength on the reduction of Fe(VI) is somewhat insignificant as with even upto 1000 times increase in ionic strength ($NaNO_3$), the reduction of Fe(VI) was almost unaffected upto 180 mins of contact. Similarly, the Zn(II)-NTA degradation by Fe(VI) was not affected by the presence of completely oxidized background electrolytes, *viz.*, ClO_4^-, NO_3^-, SO_4^{2-}, PO_4^{3-} as well as redox insensitive anions such as Cl^-. However, in presence of partially oxidized meta stable anions , *viz.*, SO_3^{2-} and NO_3^-, the reduction of Fe(VI) is found to be greatly suppressed. Hence, these results infer that a competitive reduction might occur between Zn(II)-NTA and Na_2SO_3 or $NaNO_2$ in the reaction with Fe(VI) and that Fe(VI) could more favorably react with Na_2SO_3 or $NaNO_2$ rather than Zn(II)-NTA.

Therefore, it is to be concluded that the unique multifunctional characteristics of ferrate(VI) is fully exploited effective treatment of waste waters contaminated with the organic pollutants viz., IDA, NTA and EDTA in its single form as well as in its complexed species viz., M(II)-IDA, M(II)-NTA and M(II)-EDTA. The Fe(VI) treatment is efficient in the decomplexation and degradation of the organic pollutants and the reduced Fe(VI) into Fe(III) is an excellent coagulant/flocculent to remove simultaneously the non-degradable impurities i.e., heavy metal toxic ions. Therefore, the multifunctional use of Fe(VI) is likely to reduce the input cost of the waste water treatment. Further, the ferrate(VI) treatment is devoid of any toxic bye-products, which further indicated that Fe(VI) is one ofthe ‘Green Chemicals’ and the Fe(VI) based treatment process is, perhaps, a ‘Green Technology’. The batch reactor input data may be useful in the large scale or Pilot Plant level treatment of the wastewaters contaminated with these potential water pollutants.

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List of Publications

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LIST OF PUBLICATIONS

A. JOURNALS

1. J. K. Yang, Diwakar Tiwari, M. R. Yu, **Lalramnghaki Pachuau** and S. M. Lee. Applications of ferrate(VI) in the treatment of industrial wastes containing Zn(II)-NTA complexes in aqueous solutions : a green chemical treatment, ***Environmental Technology,*** **31** (2010), 791-798.
2. M.R. Yu, Y.Y. Chang, Diwakar Tiwari, **Lalramnghaki Pachuau**, S. M. Lee & J.K. Yang. Treatment of wastewater contaminated with Cd(II)-NTA using Fe(VI), ***Desalination & Water Treatment,*** **50** (2012), 43-50**.**
3. **Lalramnghaki Pachuau**, Diwakar Tiwari, S.M. Lee. Ferrate(VI) in wastewater treatment contaminated with metal(II)-iminodiacetic acid complexed species, ***Chemical Engineering Journal*** , **230** (2013), 141-148.

B. CONFERENCE / SYMPOSIUMS

1. **Lalramnghaki Pachuau**, Diwakar Tiwari, Seung Mok Lee.. Fe(VI): A green chemical for the treatment of industrial wastes contaminated with Cu(II)-EDTA. National Conference on Green Chemistry (NCGC-2009), 6th-8th February, 2009. Department of Chemistry, Veer Narmad South Gujarat University, Surat-395007.
2. **Lalramnghaki Pachuau**, Diwakar Tiwari, Seung-Mok Lee, Sang-II Choi and Jae-Kyu Yang. Treatment of Cd(II)-NTA complex in Aqueous wastes using Fe(VI): A Green Treatment. Proceedings of American Society of Civil Engineers/ Environmental and Water Resources Institute; 3rdInternational Perspective on Current & Future State of Water Resources & the Environment, January 5–7, 2010, IIT Madras, Chennai, India.
3. **Lalramnghaki Pachuau**, Diwakar Tiwari. Fe(VI): A green oxidant for the degradation of Cd(II)-NTA complexes in wastewater. National Seminar cum Training Program on Green & Environmental Chemistry, Chemistry Department, Mizoram University, 30th March 2011.
4. **Lalramnghaki Pachuau**, C. Laldawngliana, Diwakar Tiwari and Seung Mok Lee. Organo – inorgano – sericite, the promising adsorbent for waste water treatment. Proceedings of International Conference on Advances in Environmental Chemistry (AEC-2011), 16th-19th November, 2011, Mizoram University, Aizawl, Mizoram, India.

5. **Lalramnghaki Pachuau**, Lalsaimawia Sailo, Diwakar Tiwari. Fe(VI): An efficient and green oxidant in the treatment of wastewaters contaminated with Cu(II)-IDA s(AOP-2012), 5th – 8th October 2012, M.G University, Kottayam , Kerala, India.
6. **Lalramnghaki Pachuau**, Diwakar Tiwari and Seung Mok Lee. Treatment of wastewater contaminated with Metal(II)-IDA complex species using Ferrate(VI): A green Treatment Process. The 9th Asia Pacific Conference on Sustainable Energy and Environmental Technologies (APCSEET,2013), 5th -8th July 2013, Narita Airport, Japan.

This article was downloaded by: *[Lee, Nae-Hyun][Lee, Seung-Mok]*
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Environmental Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t791546829

Application of Fe(VI) in the treatment of Zn(II)-NTA complexes in aqueous solutions

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Online publication date: 19 May 2010

To cite this Article Yang, J. , Tiwari, D. , Yu, M. , Pachuau, L. , Kim, W. andLee, S.(2010) 'Application of Fe(VI) in the treatment of Zn(II)-NTA complexes in aqueous solutions', Environmental Technology, 31: 7, 791 — 798

To link to this Article: DOI: 10.1080/09593331003664854

URL: http://dx.doi.org/10.1080/09593331003664854

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Environmental Technology
Vol. 31, No. 7, June 2010, 791–798

Application of Fe(VI) in the treatment of Zn(II)-NTA complexes in aqueous solutions

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(*Received 25 March 2009; Accepted 31 January 2010*)

The higher oxidation state of iron, i.e. Fe(VI), was exploited to treat the synthetic wastewater containing Zn(II)-NTA. The decomposition of Zn(II)-NTA by Fe(VI) was investigated with the help of analytical data obtained for the change in Fe(VI) concentration, dissolved organic carbon (DOC) and total soluble Zn(II) concentration as a function of time at various concentrations of Zn(II)-NTA and at constant Fe(VI) concentration. The UV-Visible data was used to explain the reaction kinetics for redox reactions between Fe(VI) and Zn(II)-NTA. The pseudo-first-order rate constant was calculated keeping the Zn(II)-NTA concentration in excess and hence the overall second-order-rate constant was obtained. Fe(VI) reduction was almost unaffected with the 1000 times increase in ionic strength ($NaNO_3$), as well as in the presence of completely oxidized background electrolytes. However, Fe(VI) reduction was greatly affected in the presence of both SO_3^{2-} and NO_2^- especially at higher concentrations, indicating a competitive reduction took place between Zn(II)-NTA and Na_2SO_3 or $NaNO_2$ in the Fe(VI) treatment. These results were again supported by the dissolved organic carbon observations since relatively very low removal of the dissolved organic carbon occurred in the presence of Na_2SO_3 and $NaNO_2$.

Keywords: adsorption; Fe(VI); reduction; Zn(II)-NTA

Introduction

Recently, the higher oxidation state of iron, i.e. Fe(VI), has received increased attention because of its relatively high redox potential (E^0). Because E^0 of FeO_4^{2-}/Fe^{3+} and $FeO_4^{2-}/Fe(OH)_3$ are 2.20 and 0.72 at pH 1 and 14, respectively, this enables it to act as a potential oxidizer for the degradation of even very stable organic/inorganic impurities contaminated in wastewaters [1–4].

Moreover, the Fe(VI) treatment process possesses no harmful/toxic by-products and hence may be called the ‘green treatment’ and Fe(VI) can be called the ‘green chemical’ [5–8]. Chlorination and ozonation are commonly used chemical processes in the treatment of organic compounds in waste/effluent waters. However, such treatments occur with the associated trihalomethanes [9] and bromate [10], which are considered to be harmful disinfectant/disinfection by-products (DBPs); hence their applications are limited for these treatments. Moreover, additional coagulant/adsorbents are required to remove the non-degradable impurities such as metal ions. Hence, Fe(VI) may be applied as a potential alternative for such waste/effluent water treatments. Although Fe(VI) has been studied for many years, cost comparison between Fe(VI) and other oxidation techniques such as chlorination and ozonation is limited because the supply of Fe(VI) on a commercial basis is only now available. The role of Fe(VI) is unique as it possesses multifunctional properties, i.e. relatively very high oxidizing capacity that may lead to the degradation of even very stable organic compounds; it is a potential disinfectant; and furthermore, the reduced species of Fe(VI), i.e. Fe(III), is one of the potential coagulants/adsorbents for the removal of soluble metal ions [11–13]. In addition, its role in environmental remediation, particularly the oxidative transformations and treatment of pharmaceuticals contaminated wastewaters, has been well reviewed previously [14].

Nitrilotriacetic acid (NTA) has many commercial applications, but it is used primarily as a chelating agent and as a laundry detergent builder. The compound is used to sequester Mg and Ca ions present in hard water, thereby reducing build-up and scaling caused by the salts of these ions [15]. In the late 1960s, NTA generally replaced phosphates in commercial detergents [16]. Although use of NTA in detergents was suspended in the USA in 1971, this use resumed in the 1980s after the banning of phosphorous banned from detergents. NTA was then used as an eluting agent in purification of rare-earth elements, as a boiler feed-water additive, in water and textile treatment, in metal plating and cleaning, and

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ISSN 0959-3330 print/ISSN 1479-487X online

DOI: 10.1080/09593331003664854
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in pulp and paper processing [15,17]. To a lesser extent, the compound is used in leather tanning, photographic development, synthetic rubber production, the manufacture of pharmaceuticals, and in herbicides formulations and micronutrient solutions in agriculture [16,18].

NTA itself is reasonably anticipated to be a human carcinogen on sufficient evidence of carcinogenicity in experimental animals [15,17,19,20]. When administered in the diet, NTA induced kidney tubular cell adenocarcinomas in mice of both sexes, kidney tubular cell adenocarcinomas or adenomas in male rats, papillomas or adenomas of the ureter in male rats, and transitional cell carcinomas of the urinary bladder in female rats. Increased incidences of pheochromocytomas of the adrenal gland and heptocellular adenomas were also reported for female rats.

The objective of this research is to investigate the applicability of Fe(VI) in the treatment of the synthetic wastewaters containing both NTA and Zn(II) ions. The application of Fe(VI) may induce the decomplexation of the Zn(II)-NTA complex, followed by the degradation/oxidation of NTA and the simultaneous removal of free Zn(II) from aqueous solutions, with subsequent processes such as precipitation or adsorption by the reduced Fe(III). Removal of Zn(II)-NTA by Fe(VI) is obtained with experimental data of remaining Fe(VI), dissolved organic carbon (DOC) and total soluble Zn(II) as a function of time at increased dose of Zn(II)-NTA. Reduction kinetics of Fe(VI) is studied in a batch reactor in the presence of various background electrolytes having different ionic strengths and the molar ratio of Zn(II)-NTA/Fe(VI).

Methodology

Material

$Zn(NO_3)_2 \cdot 6H_2O$: GR grade was obtained from Samchun Pure Chem. Co., Korea and nitrilotriacetic acid was obtained from Acros Organics, USA. The water (18 MΩ cm) used for sample preparations was purified using a Milli Q-Plus Instrument (Millipore SA 67120, Molshiem, France). The stock solutions (1.0 mol/L) of zinc and NTA were prepared using the same water. The stock solutions were further diluted as and when required. All other chemicals used were AR/GR grade unless otherwise mentioned.

Preparation of potassium ferrate

Potassium ferrate was prepared by adopting the method with some modifications as described in the previous research [21–23]. The purity of the dried potassium ferrate(VI) was checked by preparing an aqueous solution at pH 9.2 (phosphate buffer) and measuring the absorbance at 510 nm using a UV-Visible spectrophotometer (Optizen 2120UV, Macasys Co., Korea). The purity of the Fe(VI) was above 95% which was calculated from the usual Lambert and Beer law using the standard molar absorbance 1150 M^{-1} cm^{-1} [6].

Method

A known volume of concentrated Zn(II)-NTA solution (1 mol/L) was mixed with phosphate buffer solution (pH 9.2) to prepare synthetic wastewater containing Zn(II)-NTA ranging from 1.0×10^{-4} mol/L to 1.0×10^{-2} mol/L. As the Fe(VI) stability rapidly decreased as the solution pH decreased due to the self-decomposition of Fe(VI) as well as ease of measurement of remaining Fe(V) concentration using a UV-Visible spectrophotometer, all experiments were performed at pH 9.2 [22]. The necessary self-decomposition correction for Fe(VI) was performed with the blank.

In each solution, a known amount of Fe(VI) was introduced into it under the stirring condition. At a constant time interval, a portion of sample was removed from the reactor and then a concentrated quenching solution (2.0 mol/L Na_2SO_3) was added into each sample. The change in concentration of Fe(VI) as a function of time was checked with the help of UV-visible spectrophotometer (UV-1601, Shimadzu, Japan). Similarly, the change in total zinc concentration was checked after filtration of Fe(VI) treated samples using 0.45 μm syringe filter and was analysed by an inductively coupled plasma (Optima 2000 DV, Perkin-Elmer). The degradation of NTA was measured by TOC (total organic carbon) analyser (Shimadzu 5000). The pH measurement was done using Orion pH meter unit 720A, USA.

Results and discussion

Removal of Zn(II)-NTA as a function of time

The decomplexation of Zn(II)-NTA was carried out at pH 9.2 with the variation of Zn(II)-NTA concentration and the Fe(VI) dose 1×10^{-4} mol/L. The reason for performing reactions at pH 9.2 is in the stability of Fe(VI). From our previous research, we know that Fe(VI) stability rapidly decreased as the solution pH decreased due to the self-decomposition of Fe(VI) [22]. For example, at pH~5, after 420 seconds, the colour of the solution became yellow, due to the complete decomposition of Fe(VI) to Fe(III). Hence, no more absorbance data were recorded after 420 seconds at this pH. The sample solutions were stirred for 180 mins and then analysed for the remaining Fe(VI) concentration using UV-Visible spectrophotometer and the results obtained were shown graphically in Figure 1. The blank data was obtained in the absence of Zn(II)-NTA, which

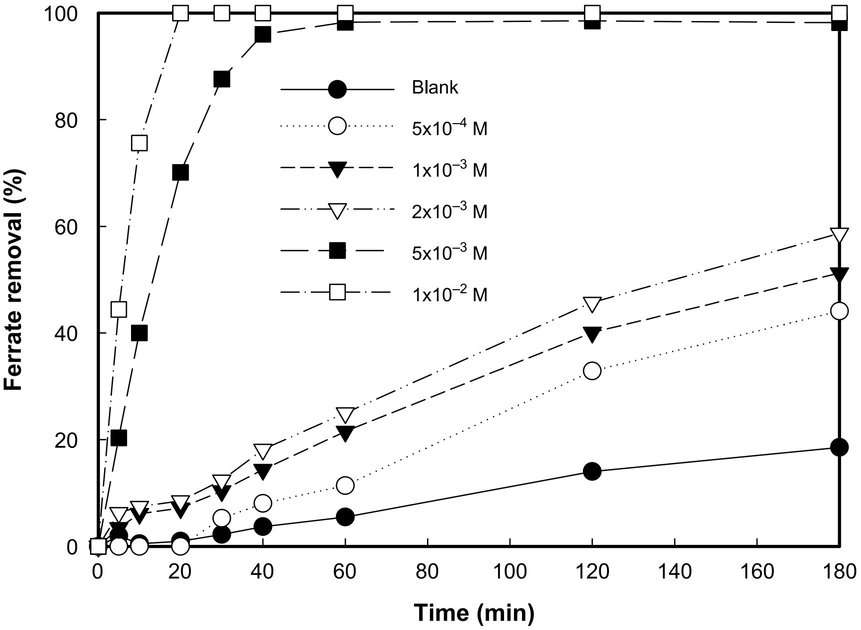

Figure 1. Percentage reduction of 1×10^{-4} mol/L Fe(VI) at five different Zn(II)-NTA concentrations as a function of time.

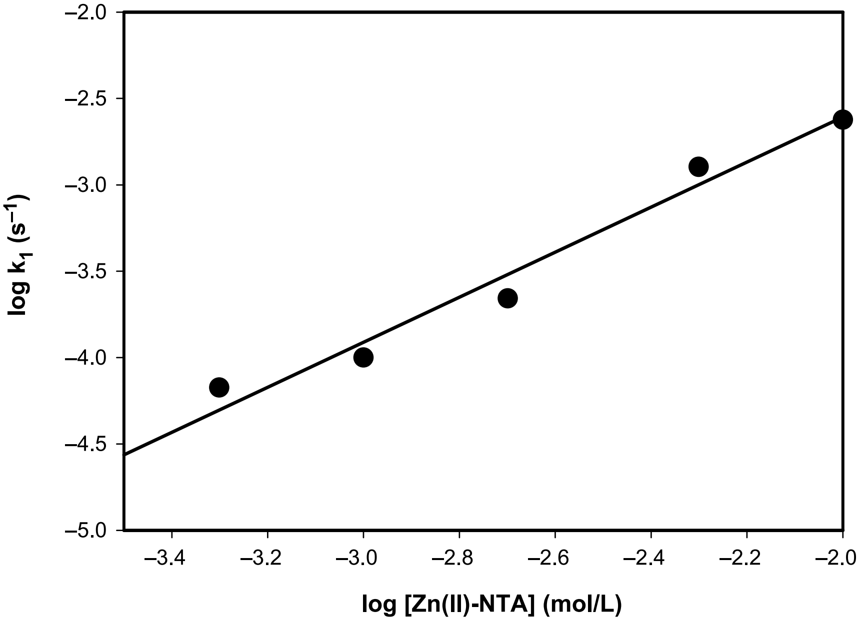

Figure 2. A linear correlation between log(k_1) and log[Zn(II)-NTA].

showed a slight removal/degradation of Fe(VI); this perhaps occurred through the self-decomposition of Fe(VI) [22].

When Fe(VI) reacts with Zn(II)-NTA, it can oxidize NTA molecules and produce several intermediates and/or final products. In this reaction, as the reduction efficiency of Fe(VI) is highly related with decomplexation efficiency of Zn(II)-NTA, the following simple irreversible reaction, expressed with Equations (1) and (2), which were previously used in the kinetic study of Cu(II)-EDTA by Fe(VI) [19], were also used in this study. Tiwari *et al.* [23] reported a quantitative kinetic information for the decomplexation of Cu(II)-EDTA in aqueous phase using Equations (1) and (2). Moreover, the decomplexation kinetics of Zn(II)-NTA was supposed to be similar to that of Cu(II)-EDTA, hence similar equations were used to analyse the kinetics of decomplexation process.

$$\mathrm{Fe(VI) + Zn(II){-}NTA \rightarrow Fe(III) + Products} \quad \ldots(1)$$

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k[\mathrm{Fe(VI)}]^{m}\,[\mathrm{Zn(II)-NTA}]^{n} \quad \ldots(2)$$

where k represents the overall rate constant of the reaction (1) and the [Fe(VI)] and [Zn(II)-NTA] are the molar concentrations of Fe(VI) and Zn(II)-NTA, respectively, m and n are the orders of the reaction with respect to the each reactant. Since, the concentration of Zn(II)-NTA (10^{-2} mol/L), at a maximum, was 100 times higher than the concentration Fe(VI), hence in this condition, we may write Equation (2) as:

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k_1[\mathrm{Fe(VI)}]^{m} \quad \ldots(3)$$

where $k_1 = k\,[\mathrm{Zn(II)\text{-}NTA}]^n$.

In order to calculate k_1 values in reaction (3), the reduced Fe(VI) concentration at a different time was fitted with either the first-order (m=1) or the second-order (m=2) equation. It was noted that for all Zn(II)-NTA concentrations, the first-order equation was better described than the second-order equation. Hence it may be said that the pseudo-first-order degradation of Fe(VI) took place. Hence, with this analysis, m may be regarded as 1. The k_1 values at five different Zn(II)-NTA concentrations are summarized in Table 1. Sharma *et al.* [24] reported that Fe(VI) oxidation of thiocyanate was well expressed by first-order with respect to Fe(VI) under pseudo-first-order conditions with SCN in excess. Noorhasan *et al.* [25] reported that both EDTA and DTPA reacted faster with Fe(V) as well as with Fe(VI) comparing to the NTA while studying the reaction between Ferrate(V)($\mathrm{Fe^{V}O_4^{3-}}$) and aminopolycarboxylates in alkaline medium by premix pulse radiolysis.

In order to calculate the ‘n’ value, log k_1 values were fitted with log [Zn(II)-NTA] concentration (cf. Figure 2). In this fitting, the ‘n’ value was calculated as 1.28, which is nearly equal to 1, hence approximately this is first-order. So it may be concluded that under the condition stated, the rate of reduction of Fe(VI) by Zn(II)-NTA was first-order for both Fe(VI) and Zn(II)-NTA; hence we may write:

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k[\mathrm{Fe(VI)}]^{1}[\mathrm{Zn(II)-NTA}]^{1} \quad \ldots(4)$$

and the pseudo-second-order rate constant (k) was obtained by the intercept of the plot, i.e. log k_1 vs. log [Zn(II)-NTA], and it was found to be 8.80×10^{-1} $\mathrm{M^{-1}\,s^{-1}}$.

The similar observations also reported by Sharma *et al.* [26] for the oxidation of uncomplexed cyanide with Fe(VI) and reported that the kinetics follows first order rate law to each of the reactant i.e., $-d[\mathrm{Fe(VI)}]/dt = k[\mathrm{Fe(VI)}]\,[\mathrm{Cyanide}]_T$. Similarly, Yngard *et al.* [27] reported the similar first order oxidation of Fe(VI) in the presence of $\mathrm{Zn(CN)_4^{2-}}$ whereas it was reported half order with respect to the $\mathrm{Zn(CN)_4^{2-}}$ complex. Hence, they estimated the overall k ($\mathrm{M^{0.5}\,s^{-1}}$); is found to be 3.56±0.13 at pH 9.1. Noorhasan and Sharma [28] reported that rate law for the reaction of Fe(VI) with EDTA was found to be first-order with respect to each reactant over the entire studied pH range. The overall rate constant, k, decreases with an increase in pH, varying from 4.19×10^{4} to 8.60×10^{-2} $\mathrm{M^{-1}\,s^{-1}}$ over the studied pH range. Similarly, the same group also studied the degradation of other complex compounds, namely, weak-acid dissociable cyanides like $\mathrm{Cd(CN)_4^{2-}}$ and $\mathrm{Ni(CN)_4^{2-}}$ with Fe(VI) at pH (9.1–10.5) [29]. They reported that the rate laws for the oxidation of these compounds may be expressed as $-d[\mathrm{Fe(VI)}]/dt = k\,[\mathrm{Fe(VI)}][\mathrm{M(CN)_4^{2-}}]^n$ where n = 0.5 and 1 for $\mathrm{Cd(CN)_4^{2-}}$ and $\mathrm{Ni(CN)_4^{2-}}$, respectively. Interestingly, here again they obtained the m=1, which is similar to our findings.

Table 1. Rate constant (k_1) for the Fe(VI) reduction at five different Zn(II)-NTA concentrations.

[Zn(II)-NTA] (mol/L)	k_1 value ($\mathrm{sec^{-1}}$)$\times10^{-4}$	Correlation coefficient (First-order)
5×10^{-4}	0.67	0.972
1×10^{-3}	1.00	0.991
2×10^{-3}	2.20	0.987
5×10^{-3}	12.7	0.979
1×10^{-2}	23.8	0.994

Effect of ionic strengths and type of background electrolytes on the reaction kinetics

Figure 3 shows the reduction efficiency of Fe(VI) at different ionic strengths with $\mathrm{NaNO_3}$ concentrations ranging from 1×10^{-3} mol/L to 1.0 mol/L at pH 9.2 as a function of time. Fe(VI) reduction was gradually increased as reaction time increased and approximately 50% of the initial Fe(VI) was reduced after 180 mins of contact. Moreover, it was also observed that even for 1000 times increase in ionic strength ($\mathrm{NaNO_3}$), the reduction of Fe(VI) was almost unaffected up to 180 mins of contact. This result suggests that $\mathrm{NaNO_3}$ does not affect on the redox reaction of Zn(II)-NTA by Fe(VI). Further, Figure 4 shows the reduction efficiency of Fe(VI) at seven different types of background electrolytes at the same concentration as a function of time. With the exceptions of $\mathrm{NaNO_2}$ and $\mathrm{Na_2SO_3}$, reduction efficiency of Fe(VI) was similar for all other employed background electrolytes over the entire reaction time. This result suggests that completely oxidized anions such as ClO_4^-, NO_3^-, SO_4^{2-}, PO_4^{3-} as well as redox insensitive anions such as Cl^- do not participate in the reduction of applied Fe(VI). Therefore Fe(VI) reduction was unaffected by the concentration of completely oxidized background electrolytes as well as not controlled by the type of background electrolytes. Meanwhile, more rapid Fe(VI) reduction was observed in the presence of SO_3^{2-} rather than NO_2^-. The greater Fe(VI) reduction by the Na_2SO_3 and $NaNO_2$ compared to the other five background electrolytes can be explained by the favourable oxidation of SO_3^{2-} and NO_2^-; these are meta-stable in oxidation state to completely oxidized SO_4^{2-} and NO_3^- states, respectively. It was reported that Fe(VI) rapidly oxidizes sulphur intermediates such as $S_2O_3^{2-}$ and SO_3^{2-} with faster rate ($t_{1/2}$ <7 s) yielding sulphate [7]. Goff and Murman used ^{18}O-enriched-ferrate tracer in studying oxidation of sulphite (SO_3^{2-}) by Fe(VI) to demonstrate that the oxygen is transferred from Fe(VI) to form sulphate (SO_4^{2-}), a reaction product [30]. The rate constant for sulphide oxidation by Fe(VI) was 1.8×10^3 M^{-1} s^{-1} at pH 9.9 [31]. The rate constant for nitrite oxidation by Fe(VI) at 25°C was 5.8×10^{-2} M^{-1} s^{-1} at pH 9.9 [26]. Similarly, the reduction of oxyiron(V) by sulphite and thiosulfate in aqueous solution was studied using premix pulse radiolysis technique [32]. Moreover, the reactions of $Fe^{VI}O_4^{2-}$ with the two sulphur radicals were also studied. The rate constants for reduction of $Fe^{VI}O_4^{2-}$ to $Fe^{V}O_4^{2-}$ by sulphite and thiosulfate radicals were reported to be $(1.9\pm0.3)\times10^8$ and $(7.5\pm0.3)\times10^7$ M^{-1} s^{-1}, respectively. These observations suggested that a competitive reduction might occur between Zn(II)-NTA and Na_2SO_3 or $NaNO_2$ in the reaction with Fe(VI). In these competitive conditions, Fe(VI) could more favourably react with Na_2SO_3 or $NaNO_2$ rather than with Zn(II)-NTA. It was again confirmed by the variation of dissolved organic carbon (DOC) concentration as a function of time at different type of background electrolytes as shown in Figure 5. The removal of DOC in presence of completely oxidized anions such as NO_3^- and PO_4^{3-} was between 40% and 60% after 3 hrs. In contrast, quite lower removal of DOC was observed in the presence of SO_3^{2-} and NO_2^-.

In order to further identify effects of the SO_3^{2-} and NO_2^- on the decomplexation of Zn(II)-NTA by Fe(VI), the reduced Fe(VI) concentration was measured as a function of time at different concentration of the SO_3^{2-} and NO_2^-. As shown in Figure 6, decreasing the concentration of both SO_3^{2-} and NO_2^- decreases the Fe(VI) reduction. This shows an interference effect of these two anions in the reduction of Fe(VI) by Zn(II)-NTA.

From the result of total Zn(II) removal after 1 and 3 hrs at different background electrolytes treated with Fe(VI) dose, i.e. 1×10^{-4} mol/L having Zn(II)-NTA 1×10^{-3} mol/L, similar removal of total Zn(II) ranging from 82 to 89% was observed for all background electrolytes. Speciation of 1×10^{-3} mol/L Zn(II)-NTA before reaction with Fe(VI) at alkaline region was calculated with the help of MINEQL geochemical software. This simulation result shows that the major soluble zinc species are ZnOH-NTA^{-2} and Zn-NTA^- at pH between

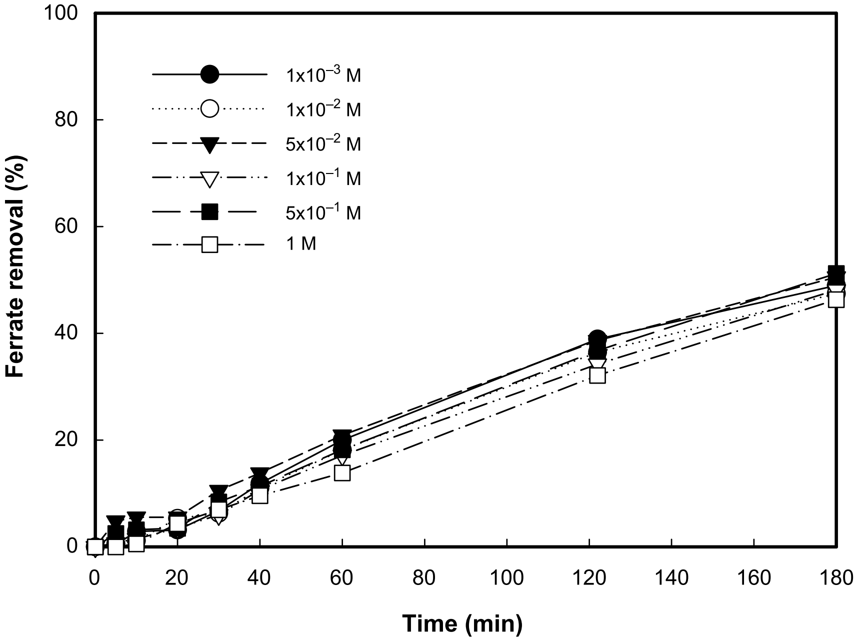

Figure 3. Reduction of 1×10^{-4} mol/L Fe(VI) as a function of time at different ionic strength with $NaNO_3$ ([Zn(II)-NTA] = 1×10^{-3} mol/L).

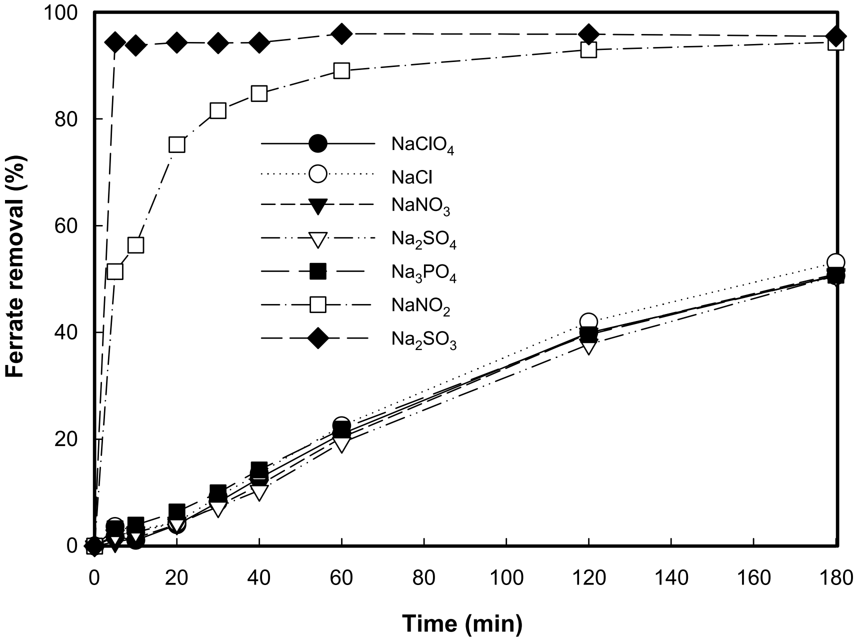

Figure 4. Reduction of 1×10^{-4} mol/L Fe(VI) as a function of time at different background electrolytes ([Zn(II)-NTA] = 1×10^{-3} mol/L).

8 and 12. As pH increased above 10.5, a fraction of the precipitated species, ZnO(active), was gradually increased. Considering this speciation, the major soluble species at pH 9.2 is identified as Zn-NTA$^-$. One possible pathway for the removal of Zn^{2+} species liberated from decomplexation of Zn(II)-NTA could be through precipitation at pH 9.2. The other possible pathway of zinc removal may be adsorption or co-precipitation on Fe(III) produced from reduction of Fe(VI). In order to elucidate removal mechanism of Zn(II) during redox reaction of Zn(II)-NTA by Fe(VI), simulation of speciation and analysis of the precipitated

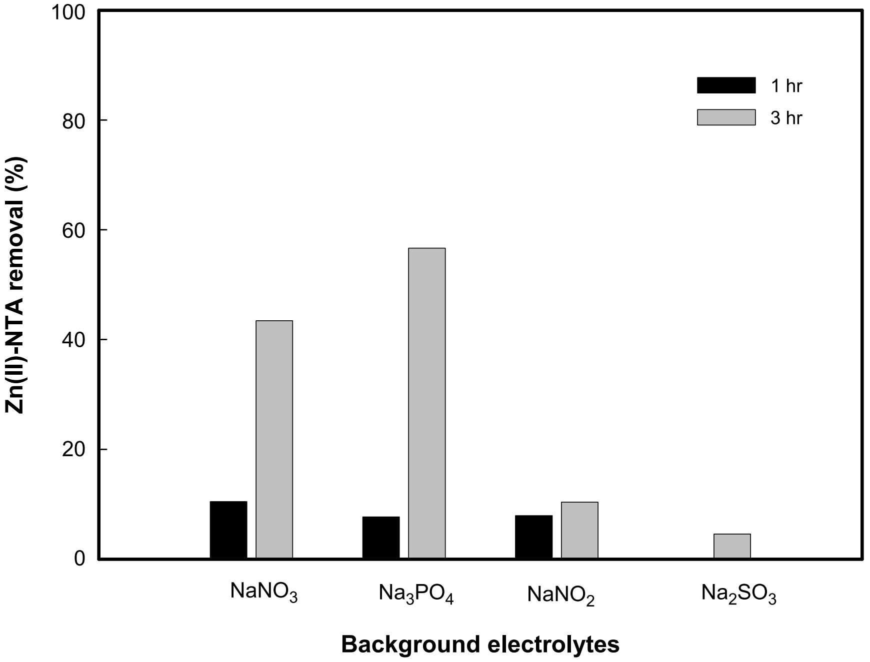

Figure 5. Variation of the dissolved organic carbon at different background electrolytes ([Fe(VI)] = 1×10^{-4} mol/L, [Zn(II)-NTA] = 1×10^{-3} mol/L).

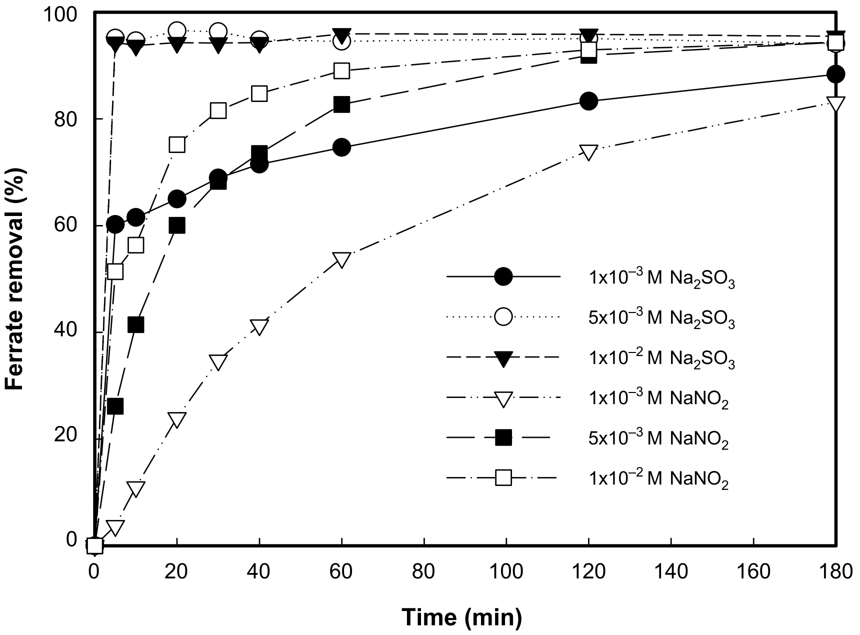

Figure 6. Reduction of 1×10^{-4} mol/L Fe(VI) as a function of time at different background electrolytes ([Zn(II)-NTA] = 1×10^{-3} mol/L).

solid was performed. From the speciation of 1×10^{-3} mol/L Zn(II) by the MINEQL geochemical software, it was found that most zinc was precipitated in solution. Also from the analysis of the precipitated solid, both Zn and Fe were measured. However, it was difficult to identify any clearer removal mechanism such as adsorption, co-precipitation and precipitation with current experimental data and simulation result due to limited information.

Conclusions

From the Fe(VI) reduction by Zn(II)-NTA, the rate of Fe(VI) reduction was first-order for both Fe(VI) and Zn(II)-NTA. The overall second-order rate constant (k) was found to be 8.80×10^{-1} M^{-1} s^{-1}. Fe(VI) reduction was almost unaffected by the 1000 times variation of ionic strength with $NaNO_3$ as well as by the presence of completely oxidized background electrolytes. However, it was greatly affected by the presence of both SO_3^{2-} and NO_2^-, especially at higher concentrations of these electrolytes. This result suggests that decomplexation of Zn(II)-EDTA can be retarded due to a competitive reduction between Zn(II)-NTA and Na_2SO_3 or $NaNO_2$ in the reaction with Fe(VI).

Acknowledgements

This work was supported by Grant R01-2006-000-10284-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

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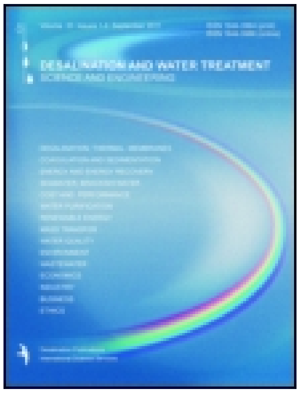

Desalination and Water Treatment
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tdwt20

Treatment of wastewater contaminated with Cd(II)-NTA using Fe(VI)

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Version of record first published: 17 Dec 2012.

To cite this article: M.R. Yu , Y.Y. Chang , Diwakar Tiwari , L. Pachuau , S.M. Lee & J.K. Yang (2012): Treatment of wastewater contaminated with Cd(II)-NTA using Fe(VI), Desalination and Water Treatment, 50:1-3, 43-50

To link to this article: http://dx.doi.org/10.1080/19443994.2012.708534

Desalination and Water Treatment
www.deswater.com

50 (2012) 43–50
December

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doi: 10.1080/19443994.2012.708534

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Treatment of wastewater contaminated with Cd(II)–NTA using Fe(VI)

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Received 21 November 2011; Accepted 7 May 2012

ABSTRACT

The aim of the present investigation is to assess the applicability of Fe(VI) in the treatment of simulated wastewater contaminated with Cd(II)–nitrilotriacetic acid (NTA) soluble species as a cleaner and greener treatment technology. Initially, the degradation of NTA was observed in a single system treatment reactor that applied varied doses of NTA. Results were correlated with the change in Fe(VI) concentration measured by UV–visible spectrophotometer. As a next step, the Fe(VI) was introduced in the reaction reactor containing Cd(II)–NTA species as to investigate the degradation of NTA measured with the help of change in total organic carbon (TOC). The NTA degradation was observed by using the TOC values obtained at different time intervals at pH 10.0. Moreover, the treated samples were subjected to the change in total cadmium concentration as to observe the simultaneous removal of cadmium from the aqueous solutions. The reactivity of the Fe(VI) was also assessed varying the pH from 8.0 to 12.0 in the treatment of Cd(II)–NTA solution.

Keywords: Fe(VI); Cd(II); NTA; Oxidation; Reduction

1. Introduction

One of the increasing concerns in the treatment of wastewaters perhaps comes from the metal complexed contaminants because of its stability and mobility in aqueous media. Several industrial processes are reported to include the wide use of chelating agents such as nitrilotriacetic acid (NTA), iminodiacetic acid, ethylenediaminetetraacetic acid, etc. These chelating agents show strong affinity towards several toxic heavy metal ions and readily form stable complexes with these metals in aqueous solutions. The degradation of these complexed species was found to be a daunting task in the wastewater treatment technology.

NTA is an important chelating agent which shows several industrial applications. It is extensively used for scale control in cleaners, water softening and in laundry detergents as a builder to replace phosphates. The use of NTA was restricted by legislation in some countries owing to their contribution to the eutrophication of lakes and ponds. In Western Europe, at least 80% of NTA is used in detergents. It is widely used as an eluting agent in purification of rare-earth elements, as a boiler feed-water additive, in water and textile treatment, in metal plating and cleaning, and in pulp and paper processing [1]. It is present in drinking water primarily in the form of metal complexed form, rather than as the free acid. The amount of NTA complexed with metal ions is dependent on the concentrations of

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*Corresponding author.

the metal ion, NTA^{3-} and H^+, as well as the formation constants of the various complexes [2].

On the other hand, cadmium is one of potential environmental pollutant that possessed greater biotoxicity towards humans and animals. In the human body, cadmium accumulates mainly in the kidneys. At high levels, it can reach a critical threshold and can lead to serious kidney failure. Cadmium metal and cadmium compounds are used as pigments, stabilizers, coatings, specialty alloys, electronic compounds, but, most of all (more than 80% of its use), in rechargeable nickel–cadmium batteries. Variety of cost effective materials suggested in the removal of Cd(II) or even other heavy metal toxic ions from aqueous solutions performed under the sorption process seems perhaps an alternative way of waste/effluent treatment [3–9]. However, the removal of metal-complexed species seems to be difficult although few reports intended to employ the materials viz., titaniumoxide in the removal of some heavy metal complexed species from aqueous solutions [10–12].

Further, due to its high chelating capacity, NTA sequesters with metal ions forming metal complexes. It was found that certain NTA complexes (Cu, Ni, Cd, Hg) were very resistant to degradation [13]. Therefore, industrial wastewater containing Cd–NTA complexes need to be treated adequately prior to its discharge into the environment.

Ferrate (Fe(VI)), a higher oxidation state of iron is one of the promising multi-purpose water treatment chemicals because of its novel properties such as high oxidizing capacity (redox potentials, 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 and 14, respectively), selective reactivity, stability as salt forms, and non-toxic decomposition by-products of ferric ion. Since Fe(VI) treatment is not associated with any toxic by-products hence it is termed as a "green compound" and the treatment process is known as "Green Process" [14–17]. Moreover, the by-product of Fe(VI); i.e. Fe(III) is one of potential coagulant/adsorbents hence, could remove other non-degradable impurities from the wastewaters. Therefore, the use of Fe(VI) in the wastewater treatment is multifunctional, it replaces several chemicals frequent to be used in wastewater treatment technology. Owing to this unique multifunctional properties, Fe(VI) has gained enhanced interests for its potential applications in the water treatment technology. Fe(VI) can effectively oxidize several stable organic compounds viz., benzene, chlorobenzene, allylbenzene, phenol, etc. [18–19] along with the inorganic contaminants viz., cyanide, ammonia, etc. [20]. Other studies revealed that Fe(VI) is used as coagulant for removing dissolved color compounds [21]. Although Fe(VI) has been shown to be effective and efficient for the removal of organic and inorganic impurities, only limited studies focused on the metal complexed systems. Yngard et al. attempted the oxidation of weak-acid dissociable cyanides, $Cd(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$, with ferrate [22]. The kinetics of the dissociation of these weak acid dissociable cyanides was discussed with pH range 9.1–10.5 and temperature range 15–45℃. It is suggested that Fe(VI) is effective in removing cyanide in coke oven plant effluent, where organics are also present. The Zn–NTA complex was treated using the Fe(VI). The possible degradation of NTA along with the simultaneous removal of Zn(II) by coagulation/adsorption process was demonstrated. Further, the effect of various background electrolyte concentrations was studied in the treatment method [23].

In view of the above the present study aims to explore the applicability of Fe(VI) in the treatment of wastewater contaminated with Cd(II)–NTA complexes through oxidation of NTA and subsequent removal of Cd(II) by reduced Fe(III) or by precipitation.

2. Methodology

2.1. Materials

The AR/GR grade chemicals were used in this study. Sodium hypochlorite (CAS# 7681-52-9), purified Fe(III) nitrate hexahydrate (CAS# 7782-61-8), potassium hydroxide (CAS# 1310-58-3), *n*-hexane (CAS# 110-54-3), anhydrous ether (CAS# 60-29-7), and methanol (CAS# 67-56-1) were obtained from Merck. Cadmium nitrate tetrahydrate (98%, CAS# 10022-68-1) and NTA (CAS# 139-13-9) were obtained from Sigma–Aldrich. Whatman filter paper (GF/C) (England) and Fritted funnel (10–15 μm) (Merck) were used. Purified water (18 MΩ cm) obtained from Milli Q-Plus Instrument (Millipore SA 67120, Molshiem, France). The stock solutions of cadmium and NTA (1.0 mol/L) were prepared in distilled water, which were further diluted as and when required.

2.2. Preparation of potassium ferrate $K_2Fe^{(VI)}O_4$

Potassium Fe(VI) was prepared by adopting wet chemical oxidation method, with some modifications as described elsewhere [24,25]. In this method, commercially available sodium hypochlorite (12–14%) was used. 300 mL of chilled NaClO solution was taken in a beaker and 90 g of solid KOH was added slowly in this solution and the resulting suspension was cooled. The precipitate formed was filtered with GF/C filter paper, the filtrate received was a clear yellow and highly alkaline NaClO solution. Again the solution was chilled and filtered using a GF/C filter paper to remove any precipitates occurred within the solution. To this solution, 20 g of pulverized ferric nitrate was added slowly within 30 min, with constant and vigorous stirring under cooling conditions (<8˚C). Further, after the complete addition of ferric nitrate, the solution was stirred for another 30 min. It was noted that the cold and highly alkaline conditions favored the oxidation of Fe(III) to Fe(VI). Also the time allowed for stirring may result in enhanced yield, even when using relatively low concentration of NaClO (i.e. 12% NaClO). The color of the solution readily changed to purple. Further, approximately 50 g of solid KOH was added slowly, ensuring that the solution temperature should not rise above 15˚C as it may cause decomposition of Fe(VI). The solution mixture was allowed to cool by standing in a refrigerator for 40 min. The resulting dark purple slurry was filtered with a glass filter (medium porosity 10–15 μm), and the filtrate was discarded. The precipitate was washed with 100 mL of cold/chilled 3 M KOH solution. The filtrate from the washings was collected, taken into a flask and 100 mL of saturated chilled KOH solution was then added. The potassium ferrate readily precipitated, which was filtered again with a GF/C filter. The filtrate was discarded, and the solid was washed with 50 mL of cold 3 M KOH solution, and the filtrate was collected in a beaker. Similarly, re-precipitation was carried out at least 3–4 times to remove any impurities, if present. Finally, the solid was flushed with n-hexane (4×10 mL), dry methanol (2×5 mL) and diethyl ether (2×10 mL). The final product was collected carefully, it was almost black in color and stored in vacuum desiccator. Further, the purity of the product was assessed using UV–visible measurement since the standard molar absorbance of Fe(VI) solution was reported to be 1150 M^{-1} cm^{-1} at 510 nm at pH ~ 9.2 [26]. The purity of the synthesized Fe(VI) was found to be >95%.

2.3. UV–visible measurements

Using a UV–visible spectrophotometer (Thermo Electron Corporation, England; Model: UV1), indirectly the degradation of NTA was observed by observing the change in Fe(VI) decomposition. The known concentration of NTA with constant pH (obtained by the phosphate buffer) was taken in a beaker and the known amount of solid Fe(VI) was then added to this solution. Further, the change in absorbance was recorded with time using the UV–visible spectrophotometer at 510 nm. Absorbance of blank solutions, i.e. the Fe(VI) solution (same pH obtained by phosphate buffer) was also recorded simultaneously at 510 nm for necessary absorbance correction. The decrease in absorbance is mainly due to the degradation of NTA in solution. Similar methodology was employed in the degradation of cyanide or other pollutants using Fe(VI) earlier [20,24].

2.4. TOC measurements

Total organic carbon analysis was performed to indicate the degradation level of NTA. Cd(II)–NTA solution (1.0×10^{-4} mol/L) was prepared and a known amount of Fe(VI) was added as to obtain the concentration of Fe(VI) in solution as 1.0×10^{-4} or 2.0×10^{-4} mol/L with constant stirring and at constant pH 10.0 (phosphate buffer). The solutions were stirred constantly maximum for 2 h, and while stirring the aliquots were taken intermittently at different time intervals as to measure the total organic carbon content using TOC analyzer (TOC-5000A, Shimadzu, Japan). The blank solutions were also analyzed for TOC for necessary corrections. Hence, the corrected values inferred to the degradation of NTA in solution.

2.5. Inductively coupled plasma measurements

Similar to the TOC data, the removal of Cd(II) following the degradation of Cd(II)–NTA complex by Fe (VI) was studied by analyzing the total cadmium concentration in the treated solutions using an inductively coupled plasma (Optima 2000 DV, Perkin–Elmer, USA). Cd(II)–NTA complex (1.0×10^{-4} mol/L) was treated with different dosages of Fe(VI) (1.0×10^{-4} mol/L and 2.0×10^{-4} mol/L) and the solutions were constantly stirred in reaction reactors.

The aliquots were taken out at different time intervals, filtered quickly using 0.45 μm syringe filter and subjected to the Cd(II) concentration using ICP. The removal of Cd(II) was calculated as in percentage obtained by using the formula given below:

$$\%\ \text{Removal} = ((C_0 - C_t)/C_0) \times 100$$

where C_0 is the initial concentration of Cd(II) taken and C_t is the concentration of Cd(II) at time "*t*."

Further, the simultaneous removal of cadmium (*cf.* reaction 5) was observed using the ICP analysis. The Cd(II)–NTA (1.00×10^{-4} mol/L) was treated with two different dosages of Fe(VI), i.e. 1.0×10^{-4} and 2.0×10^{-4} mol/L at constant pH 10.0. Solutions were continuously stirred in the reaction reactor, intermittently the aliquots were withdrawn and filtered with 0.45 μm syringe filter and subjected to the total cadmium analysis using ICP. Results obtained are converted into the percent removal of cadmium and shown in Fig. 5.

2.6. pH dependence study

The 5.0×10^{-4} mol/L of Cd(II)–NTA solution was prepared having the pH of 8, 9, 10, 11 and 12 separately using phosphate buffer and were taken in a reaction reactor. A known amount of Fe(VI) was added in the reactor to achieve the Fe(VI) concentration 1.0×10^{-4} mol/L in solution. The solutions were stirred and the change in absorbance was observed as a function of time. Further, after continuous stirring for ca. 2 h the solutions were filtered using 0.45 μm syringe filter and subjected to its Cd(II) analysis using ICP.

2.7. Kinetics models and data analysis

The studied reduction kinetic data of Fe(VI) by NTA were analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations. In order to obtain rate constants, a linear form of each rate equation was applied. A linear regression line has an equation of the form $Y = a + bX$, where X is the explanatory variable and Y is the dependent variable. The slope of the line is b, and a is the intercept. This experiment was repeated three times and the average values including standard deviations were reported.

3. Results and discussion

3.1. Species of $Fe^{(VI)}O_4^{2-}$ in aqueous solution

Several spectroscopic studies enabled that various protonated and deprotonated species of Fe(VI) are present in solution and these species are predominant at different solution pH, which basically depends on the acidic dissociation constant of that particular species. Fig. 1 depicts the percentage speciation of these species with the function of pH. The speciation was carried out using the known pK_a's values, i.e. $pK_{a1} = 1.6$, $pK_{a2} = 3.5$, and $pK_{a3} = 7.3$ of $Fe^{(VI)}O_4^{2-}$ [14,25]. Fig. 1 clearly indicated that $HFeO_4^-$ and FeO_4^{2-} are predominant in neutral and alkaline pH, in which Fe(VI) was known to be relatively stable towards its spontaneous decomposition to ferric iron, Fe(III) [27]. Fig. 1 also indicated that at pH ~ 10, the only species, i.e. FeO_4^{2-} exists in aqueous solutions.

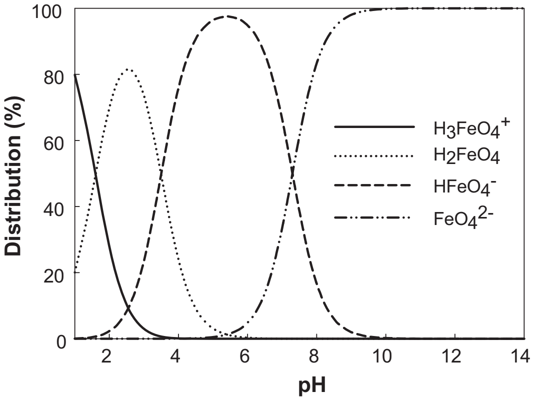

Fig. 1. Speciation of Fe(VI) species in aqueous solutions.

3.2. Degradation of NTA

The UV–visible data recorded at 510 nm were used to analyze the oxidation of NTA at different time intervals. The basic oxidation–reduction reaction involved can be written as (Eq. (1)):

$$\text{NTA} + \text{Fe(VI)} \rightarrow \text{Intermediates} \rightarrow \text{Products} + \text{Fe(III)} \quad (1)$$

The degradation of NTA was primarily observed with the change in Fe(VI) concentration in the solution using UV visible data. Hence, to observe the NTA degradation, various molar ratios of Fe(VI) to NTA were initially taken i.e. 1:0.5–1:15 and the change in absorbance (which is related to the concentration of Fe (VI)) was recorded. Then it was converted to percent reduction of Fe(VI) as shown in Fig. 2. It was noted that increasing the concentration of NTA, a gradual increase of Fe(VI) percentage reduction took place which clearly suggested more decomposition of NTA also took place. Quantitatively, it was noted that increasing the NTA concentration from 5.0×10^{-5} to

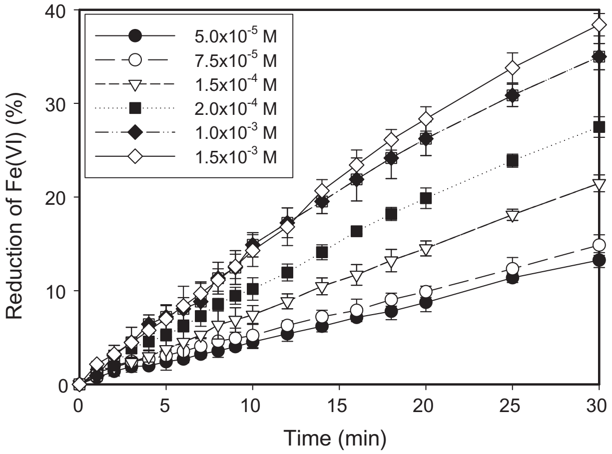

Fig. 2. Reduction of Fe(VI) as a function of time for different concentration of NTA for the constant Fe(VI) concentration 1.0×10^{-4} mol/L at constant pH 10.0.

1.5×10^{-3} mol/L, the respective percent Fe(VI) reduction was increased from 13.3 to 38.4% after 30 min keeping the Fe(VI) concentration at constant, i.e. 1.0×10^{-4} mol/L and solution pH ~ 10.0. Similar results were obtained for the decomposition of CN^- or bisphenol as treated with Fe(VI) in aqueous solutions [24,25].

The rate expression for the reaction of Fe(VI) with NTA can be written as (Eq. (2)):

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k \times [\mathrm{Fe(VI)}]^m \times [\mathrm{NTA}]^n \tag{2}$$

where [Fe(VI)] and [NTA] are the concentrations of Fe (VI) and NTA respectively; m and n are their respective order and k is the overall reaction rate constant. Kinetic studies were carried out using the data obtained for the amount of Fe(VI) degraded for various molar ratios of NTA to Fe(VI). Further, Eq. (1) may be written as:

$$-\frac{d[\mathrm{Fe(VI)}]}{dt} = k_1 \times [\mathrm{Fe(VI)}]^m \tag{3}$$

where

$$k_1 = k[\mathrm{NTA}]^n \tag{4}$$

Eq. (3) was used to deduce the rate kinetics in particular to the reduction of Fe(VI). The change in Fe(VI) concentration data obtained individually for different NTA:Fe(VI) molar ratios was used for the first and second-order rate kinetics (as taking $m = 1$ or 2) and was observed that the results were best fitted to the first order rate kinetics (i.e. $m = 1$) since the correlation coefficients (0.988–0.999) were reasonably high comparing to the correlation coefficients (0.894–0.995) obtained for the second order rate constant values (i.e. $m = 2$). Hence, it was assumed that the pseudo-first order rate kinetics was applicable to the decomposition of Fe(VI) in the presence of NTA [23,25,28]. The k_1 values were evaluated for the different molar ratios of the NTA to Fe(VI) and are returned in Fig. 3. It was observed that almost a linear relationship was observed between the k_1 and NTA concentration up to 2×10^{-4} M NTA and then increase of k_1 was much slowed down above 2×10^{-4} M NTA.

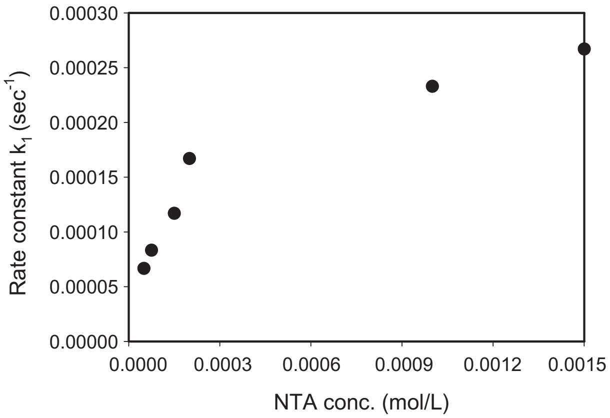

Fig. 3. Variation of k_1 value at different NTA concentration [Fe(VI): 1.0×10^{-4} mol/L; pH 10.0].

3.3. Degradation of NTA in Cd(II)–NTA system

Further, the mixed system of NTA, i.e. Cd(II)–NTA complex was taken and the decomposition of NTA in the Cd(II)–NTA was analyzed using the TOC data. The basic equation may be written as:

$$\begin{aligned}&\mathrm{Fe(VI)} + \mathrm{Cd(II)\text{–}NTA} \rightarrow \text{Decomplexation of}\\&\mathrm{Cd(II)\text{–}NTA} + \mathrm{Fe(III)} \rightarrow \text{Decomposed NTA products}\\&\ + \mathrm{Cd(II)} + \mathrm{Fe(III)}\end{aligned} \tag{5}$$

The decomplexation of Cd(II)–NTA was supposed to be a very fast step. However, the decomposition of NTA was noted to be a slow step. The TOC data were collected at various time intervals.

The mixed complex system, i.e. Cd–NTA (1.0×10^{-4} mol/L) was treated with two different dosages of Fe(VI), i.e. 1.0×10^{-4} and 2.0×10^{-4} mol/L keeping the solution pH ~ 10 as constant (phosphate buffer). The TOC values were recorded at different time intervals. Further, based on the TOC values the percent decomposition of NTA was calculated and returned in Fig. 4. Fig. 4 clearly shows that the degradation of NTA increases with increasing the contact time and achieved almost a constant value after the 60 min of contact. Further, maximum 23% of NTA was degraded at the Fe(VI) dosages of 1.0×10^{-4} and 2.0×10^{-4} mol/L. Quantitatively, within 120 min of contact, the TOC values were decreased from 7.01 to 5.40 mg/L (for 1.0×10^{-4} mol/L of Fe(VI) dosages) and 7.01 to 5.40 mg/L (for 2.0×10^{-4} mol/L of Fe(VI) dosages). It was observed that even an increase in Fe (VI) dose, the degradation of NTA was unaffected which inferred that the 1:1 stoichiometry occurred for the NTA to Fe(VI) independent to the Cd(II) presence. Previous results also demonstrated that the stoichiometric ratio obtained between total cyanide and Fe(VI)

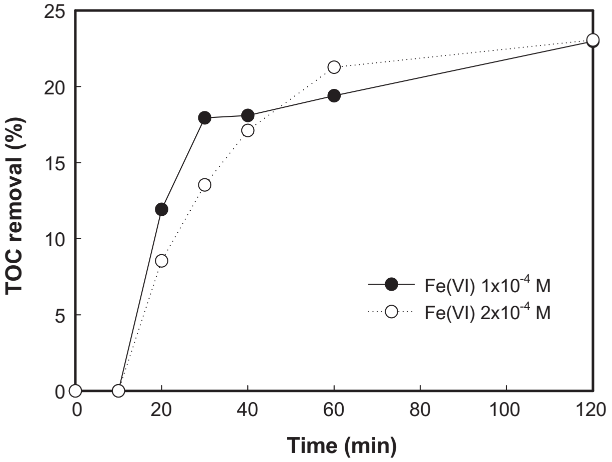

Fig. 4. Percent degradation of NTA in the complexed system of Cd(II)–NTA as a function of time [Cd(II)–NTA: 1.0×10^{-4} mol/L; pH 10.0].

was found to be 1:1 in the degradation of zinc-cyanide complex by Fe(VI) [29].

3.4. *Removal of Cd(II) by Fe(VI) as a function of time*

Fig. 5 clearly demonstrates that increasing the dosages of Fe(VI) from 1.0×10^{-4} to 2.0×10^{-4} mol/L apparently increased the removal of Cd(II) respectively from 14.9 to 23.8%. Previously, it was observed that maximum of ca. 23% of TOC was removed which was unaffected with the Fe(VI) dose. However, the simultaneous removal of Cd(II) from aqueous solutions was greatly affected with Fe(VI) dose. This increase in percent removal of Cd(II) from aqueous solution may be explicable on the basis that increasing the dose of Fe(VI) caused an increased concentration of Fe(III) in the solution which may enable an enhanced free Cd(II) removal either by the coagulation or adsorption process [30,31].

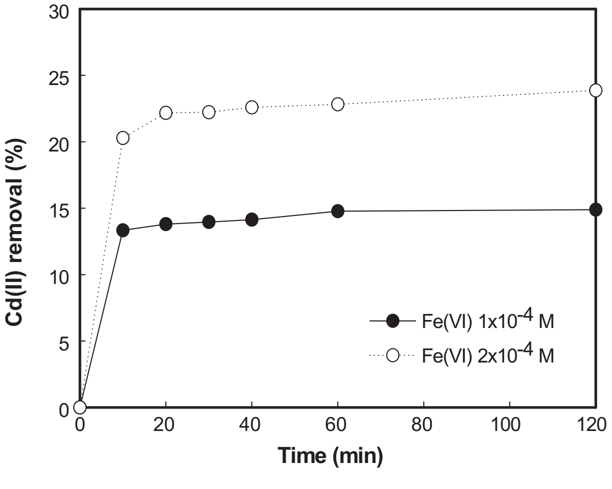

Fig. 5. Percent removal of free cadmium as a function of time for two different dosages of Fe(VI) at pH 10 [Cd(II)–NTA concentration: 1.0×10^{-4} mol/L].

Moreover, it was clearly shown (Fig. 5) that very fast removal of cadmium by Fe(VI) occurred as within few min of contact, maximum cadmium was removed. This indicated that the Fe(VI) which is one of potential coagulant/adsorbent could remove efficiently the free cadmium from aqueous solutions. Previous studies inferred that Fe(VI) could be used in the efficient removal of several cations/anions including Mn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+}, and As(III) from aqueous solutions via oxidation/coagulation/adsorption process using the lower dose of ferrate(VI), i.e. 10–100 mg/L [32,33]. Additionally, we presumed that at this pH 10.0 the free cadmium is supposed to be precipitated as insoluble $Cd(OH)_2$ and resulted in the decrease in cadmium concentration in the bulk solution.

3.5. *Treatment of Cd(II)–NTA complex by Fe(VI) as a function of pH*

The pH is an important parameter in the treatment of Cd(II)–NTA complex by Fe(VI). Hence, the study further extended to observe the pH effect (i.e. from pH 8.0–12.0 (using phosphate buffer)) in the treatment of 5.0×10^{-4} mol/L of Cd(II)–NTA solution with 1.0×10^{-4} Fe(VI) dose. The data were collected as the change of percent ferrate reduction as a function of time for different pH condition and are returned in Fig. 6(a). Fig. 6(a) clearly demonstrated that a rapid Fe (VI) reduction was observed at pH 8 in the initial reaction time but much reduced Fe(VI) reduction was noticed at a higher solution pH. This fast increase in Fe(VI) percent decomposition intended that the reactivity of Fe(VI) increases decreasing the pH as at pH 1.0 the redox potential of Fe(VI) was 2.20 V whereas it was reported to be 0.72 V at pH 14 [14–16].

Further, on the other, hand the simultaneous removal of cadmium was obtained at different solution pH and is represented in Fig. 6(b). It was clearly demonstrated that increasing the solution pH from 8.0 to 12.0 could not cause significant change in Cd(II) removal as it was below 5% for all solution pH. This may be explicable with the fact that only five times less Fe(VI) was introduced in the treatment process hence, insignificant of Fe(III) was generated to remove higher concentration of the free Cd(II) from aqueous solutions. Moreover, it was observed that relatively

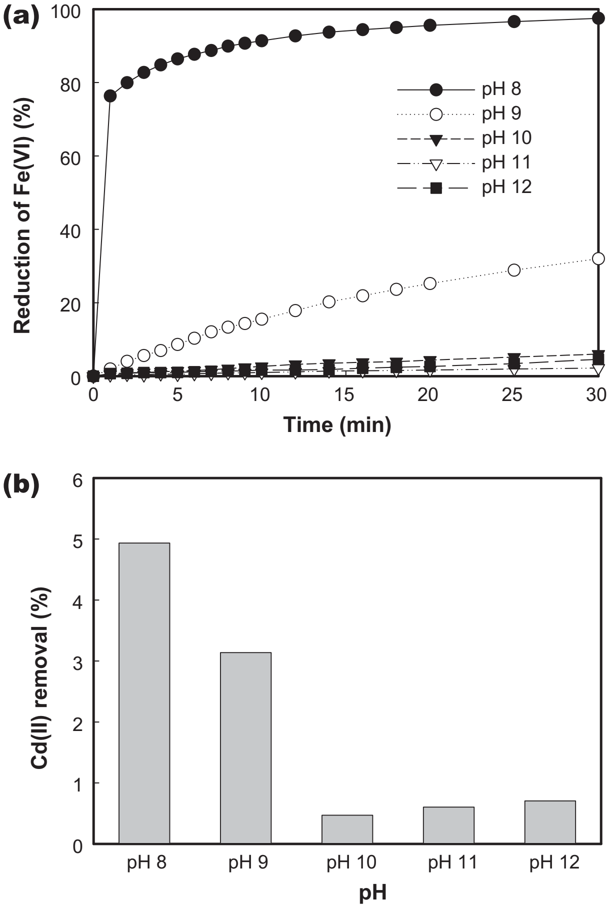

Fig. 6. (a) Reduction of Fe(VI) and (b) removal of Cd(II) as a function of time for different pH (Cd(II)–NTA concentration: 5.0×10^{-4} mol/L and Fe(VI) concentration: 1.0×10^{-4} mol/L).

higher, Cd(II) was removed at low pH, i.e. pH 8.0. This could again confer the results obtained with the Fe(VI) reduction percentage which was obtained relatively higher at lower pH values.

4. Conclusions

The Fe(VI) was prepared by the modified wet oxidation method. Further, the Fe(VI) was used for the degradation of NTA as well the complexed species of Cd(II)–NTA complex systems in an attempt to find cleaner/greener waste water treatment technologies. Fe(VI) was found to be effective for the oxidation of NTA in the single, i.e. NTA and in the complexed system, i.e. Cd(II)–NTA at pH ~ 10. The degradation of NTA in the complexed Cd(II)–NTA system obtained with the TOC data showed that maximum 23% of NTA was degraded. Further, the Fe(VI) converted into Fe(III) as in the form of ferric hydroxide can coagulate/flocculate or even by co precipitation process can remove approximately 23% of free cadmium from the aqueous solutions. pH dependence data obtained in the pH range 8.0–12.0 showed that Fe(VI) found to be more reactive at pH 8.0 than the higher pH values studied at least in the treatment of Cd(II)–NTA. The present study is a useful application of Fe(VI) in the treatment of industrial waste water contaminated with metal complexed species in particular the Cd(II)–NTA species.

Acknowledgments

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2010-0022081). One of co-author DT acknowledges partly the financial support received from DST, New Delhi (vide project No. SR/S1/IC-35/2010).

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ChemicalEngineeringJournal230(2013)141–148

Contents lists available at SciVerse ScienceDirect

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Ferrate(VI) in wastewater treatment contaminated with metal(II)-iminodiacetic acid complexed species

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highlights

- Green treatment proposed using Ferrate(VI) in the remediation of Cu(II)-IDA and Zn(II)-IDA contaminated water.
- Mineralization of IDA along with M(II) was removed simultaneously.
- Kinetics of degradation was proposed.

article info

Articlehistory:
Received11March2013
Receivedinrevisedform17June2013
Accepted20June 2013
Availableonline28June2013

Keywords:
Ferrate(VI)
M(II)-iminodiaceticacid
Decomplexation
Mineralization
Kinetics
Coagulation/flocculation

abstract

The aim of this investigation is to assess the suitability and applicability of ferrate(VI) in the treatment of wastewaters contaminated with the Cu(II)-IDA and Zn(II)-IDA (IDA: iminodiacetic acid) complexed species in an attempt to provide safe and environmentally benign treatment process. The study was conducted for the degradation of metal(II)-IDA, followed by the oxidation of IDA and simultaneous removalofmetal(II)speciesbythecoagulation/flocculation process obtainedbythereducedFe(VI)into Fe(III). The high purity of ferrate(VI) was synthesized by the wet oxidation process in the laboratory and a regulated dose was imparted to the water contained with metal(II)-IDA species in solution. The batch reactor operations were performed for various parametric studies *viz.*, effect of solution pH and metal(II)-IDA concentration for a fixed dose of ferrate(VI). The pH dependence data obtained from varying pH from 8.0 to 12.0 showed that higher efficiency of degradation of Fe(VI) was occurred at lower pH value i.e., at pH 8.0. Similarly, the total organic carbon (TOC) values showed in accordance to the UV–Vis data that the lower pH values (i.e., pH at 8.0) favored an enhanced degradation/mineralization of IDA since low TOC values were obtained at low pH values. The simultaneous removal of Cu(II) and Zn(II) was obtained through the process showed that insignificant percent of metal (Cu(II) or Zn(II)) was removed by the process which was significantly enhanced at pH 12.0. The UV–Vis data recorded at different time intervals for the reduction of Fe(VI) at varied metal(II)-IDA concentrations was utilized to demonstrate the kinetics of degradation. Further, this was employed in obtaining the overall rate constant of the degradation. These kinetic data revealed that an efficient degradation of IDA was achieved using the Fe(VI) treatment.

1. Introduction

IDAwhichisoneofamino-polycarboxylicacidhavingtwocarboxylic groups widely used as potential sequestering agents to control the metal mobility in the aquatic environment [1,2]. Becauseoftheirhighcomplexingcapability,thepolycarboxylicacids are much employed in the detergent industry as substitutes of phosphates [3,4]. It was reported that the chelating resins comprising with variety of ligands forming selective and suitable bondswithseveralheavymetaltoxicions.Thiscouldenableasuitable option for the attenuation of these metal ions from aqueous solutions [5–7]. Further, due to available electron pairs and the tendencyofformingstablecovalentcomplexeswithbivalentmetals,chelatingresinscontainedwithIDA,forinstancethecommercial products *viz.*, Rohm & Haas (Amberlite IRC748), Purolite (S930), Bayer (Lewatit TP207) or the synthesized Chelex-100 (Bio-Rad Laboratories, Richmond) were widely employed in the attenuationortrappingofseveralheavymetalions.Theextensive studies were performed for various parametric factors including pH, time, ionic-strength, temperature, adsorption equilibrium,

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http://dx.doi.org/10.1016/j.cej.2013.06.081

thermodynamics, kinetics, dynamics, competitive selectivity and regeneration [8–10]. The tap water was treated with the IDA impregnated cation exchange resins [11]; nickel loading and its selective attenuation was carried out using the iminodiacetic acid chelating resins [12,13]. Recent studies indicated that IDA is more useful in making the functionalized carbon nanotubes which have showed enhanced applicability in the sorption, pre-concentration of several heavy metal cations in a heterogeneous separation process [14]. Moreover, the silica capillaries were functionalized with the IDA and Cu(II) was immobilized in the selective proteins or peptide determination and separation. This was studied in an extension of the immobilized metal ion affinity chromatography as to make the miniaturization of the devices in the chromatographic column separation [15–17]. Additionally, the IDA widely employed as a chemical intermediates for the production of glycophosphate herbicides, electroplating solutions, chelating resin, surfactants, anticancer drugs etc. [18–22]. These diverse studies enabled the wide applications of IDA for the various detection/attenuation/separation purposes of many heavy metal toxicions. The heavy metal-IDA complexed compounds are seemingly showed an enhanced toxic effects in the water or soils and posing a serious threat towards the human being or plants. Moreover, the heavy metal-IDA complexed species showed high solubility and mobility in the aqueous solutions hence, restricted its separation from the aqueous phase by simple precipitation process.

Ferrate(VI) chemistry and its applications in the environmental remediation received a great attention in recent past because of, relatively, high oxidizing capacity. Moreover, the reduced ferrate(VI) into ferric(III) is an extremely good coagulant/flocculent which may serve as to remove the non-degradable impurity by coagulation/flocculation or even by adsorption process. Moreover, the entire treatment process is devoid of any harmful toxic by-products hence, the treatment is known as ‘Green treatment’ and Fe(VI) is termed as ‘Green Chemical’ [23–29]. The ferrate(VI) was employed previously for the treatment of metal complexed species, i.e., metal(II)-cyanide or Cu(I)-cyanide and showed a significant degradation of cyanide and simultaneous removal of metal ions by coagulation/adsorption [30–33]. Further it was employed in the treatment of electroplating industry waste contained with Cu(II) and Ni(II) complexed cyanides [34]. In a line Cu(II)-ethylenediamine tetraacetic acid (EDTA) complexed species was treated with the Fe(VI) and showed that low pH conditions favored the decomplexation/degradation of the complexed species [35]. The polycarboxylic acids complexes including Zn(II)-NTA, Cd(II)-NTA were attempted and showed that NTA (nitrilotriacetic acid) was degraded partially and the metal was removed simultaneously in part. Additionally, the presence of several background electrolyte concentrations were also studied [36,37]. Recently, the study was extended for the suitability of Fe(VI) in the treatment of Cu(II) complexes with IDA, NTA, EDTA and EDDA (ethylenediaminetetraacetate) and the order of the oxidation was assessed in terms of Fe(VI) reduction and suggested the order follow Cu(II)-EDDA > Cu(II)-IDA _ Cu(II)-NTA _ Cu(II)-EDTA which was in accordance to their respective stability constant values [38]. Further, the treatment of sulfide mine tailings were investigated as the metal-complexed sulfide was oxidized rapidly into sulfate [39]. Similarly, a study was performed in the metal-sulfide treatment [40] and indicated that a fast oxidation of metal-sulfide was affected greatly in presence of $NaNO_2$ and Na_2SO_3 background electrolytes.

Therefore, keeping in view the suitability and applicability of ferrate(VI), it was assessed in the treatment of wastewaters contained with metal complexed species. The present article is to optimize the degradation/mineralization of IDA and the simultaneous removal of Cu(II) and Zn(II) in the simulated batch reactor operations.

2. Materials and methods

2.1. Materials

Ferrate(VI) was synthesized by the known wet oxidation method as described previously [30,34,41] and the purity was checked with the standard method [42] which was found to be more than 96%. Iminodiacetic acid (IDA; $C_4H_7NO_4$) and iron(III) nitrate nanohydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were obtained from the Sigma–Aldrich. Co., USA. Potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), hydrochloric acid (HCl) was purchased from Merck, India Ltd. Product. Water was purified (10–15 MΩ cm) using Millipore Water Purification System (Model: Elix3) and employed throughout the experiments. Syringe filter of 25 mm diameter in size and porosity of 0.47 μm was obtained from Whatman, USA and was employed for filtration of treated samples. A pH-meter having glass and calomel electrode assembly (EUTECH Instruments; Model: Cyberscan pH 310, pH/MV/°C/F Data meter) was used for pH measurements.

2.2. Batch reactor studies

2.2.1. Decomplexation/degradation of Cu(II)-IDA and Zn(II)-IDA complexes

The degradation of IDA in a single system was investigated by employing constant dose of Fe(VI) 1.0×10^{-1} mmol/L having varied concentration of IDA (0.3×10^{-1} to 15.0×10^{-1} mmol/L) at various pH values ranging from pH 8.0 to 12.0 using phosphate buffer. The absorbance of the solution mixture was recorded at 510 nm for the degradation of Fe(VI) as a function of time. In parallel, a blank observation was recorded to subtract the self-decomposition of ferrate(VI) in the same medium at the same solution pH. The solution mixtures were stirred for 2 h and filtered with syringe filter and the filtrate was subjected for the TOC (total organic carbon) measurements using TOC analyzer (Shimadzu, Japan; Model: TOC-VCPH/CPN). The TOC values were further utilized to obtain the percent degradation of IDA. The blank correction was always conducted prior to calculate the percent degradation.

Similarly, the different solutions of Cu(II)-IDA or Zn(II)-IDA (0.5–15.0 mmol/L) were taken and pH was adjusted from 8.0 to 12.0 and known but constant amount of Fe(VI) (1.0 mmol/L) was introduced in the reaction reactor and the decomplexation/degradation of these complexed species were studied as in terms of Fe(VI) reduction observed by the absorbance data recorded at 510 nm. The samples were stirred further for 2 h and filtered using 0.45 μm syringe filter. The filtrates were then subjected for the TOC measurements. Moreover, the absorbance data recorded at different time intervals was utilized to discuss the kinetics involved in the overall degradation of pollutant by Fe(VI).

2.2.2. Simultaneous removal of Cu(II) or Zn(II)

The Fe(VI) treated metal(II)-complexed sample solutions were filtered using the 0.45 μm syringe filters and filtrates were collected. Part of this sample was subjected for the AAS measurements (Atomic Absorption Spectrometer; Fast Sequential Atomic Absorption Spectrometer: Model AA240FS, Varian) as to analyze the total dissolved Cu(II) or Zn(II) concentration. Moreover, a part of the filtrate sample pH was raised to 12.0 by the addition of drops of concentrated sodium hydroxide solution; and again filtered and subjected for the Cu(II) or Zn(II) estimation using AAS analysis. The aim of raising the pH was to enhance the coagulation/flocculation of the free metal ions if present in solution.

3. Results and discussion

3.1. Decomplexation and degradation of M(II)-IDA complex species

3.1.1. Effect of M(II)-IDA concentration

The decomplexation and degradation of Cu(II)-IDA and Zn(II)-IDA complexes were investigated by varying the concentration of M(II)-IDA from 0.3mmol/L to 15.0mmol/L at a constant dose of Fe(VI) 1.0mmol/L. In other words the molar ratio of M(II)-IDA/Fe(VI) was varied from 0.3:1 to 15:1. These complexed species were also treated at different pH values i.e., from pH 8.0 to 12.0. The results were shown graphically in Figs. 1 and 2 respectively, for the Cu(II)-IDA and Zn(II)-IDA system (data shown only for pH 9.0). These results clearly demonstrated that a fast reduction of Fe(VI) was occurred during the initial period of time which was slowed down in the latter period of contact time and finally attained, almost, a constant value just after 10min of time for Zn(II)-IDA and about 15–20 min for Cu(II)-IDA systems. It was further noted that increasing the molar concentration of Cu(II)-IDA, i.e., from 0.3 to 15.0mmol/L, generally, favored the decomplexation/degradation of M(II)-IDA species in solutions. This is due to more and more Fe(VI) was reduced with an enhanced rate. This suggested that increasing the pollutant concentration, could be treated effectively employing with regulated dose of Fe(VI). It was previously reported that increasing the concentration of Cu(II)-CN or Ni(II)-CN was favored in rapid removal of Fe(VI) [30] or even with a fast degradation of Cu(I)-CN complexed species as studied elsewhere [43].

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

Further, the kinetics of the reduction or the removal of Fe(VI) was carried out in the oxidation of M(II)-IDA using the time dependence absorbance data collected at different pH values and different molar ratios of Fe(VI) to M(II)-IDA. The absorbance data was then converted into the Fe(VI) concentration and utilized in the kinetic calculations. The ferrate(VI) was readily decomposed into Fe(III) through the reductive pathways [44]:

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

$$[O] + H_2O \rightarrow 2{\cdot}OH \quad (2)$$

$$2{\cdot}OH \rightarrow H_2O_2 \quad (3)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (4)$$

The generated hydroxyl free radical possessed with strong oxidizing capacity [45]. However, the reactions of Fe(VI) with several organic/inorganic pollutants in aqueous medium were found to be complicated to demonstrate; since either a direct oxidation by Fe(VI) took place or by the newly generated hydroxyl free radicals could initiate the oxidation process. The simple kinetics in degradation of M(II)-IDA was suggested by the change in Fe(VI) concentration using the absorbance data collected at 510 nm wavelength. Therefore, the basic equation for reduction of Fe(VI) could be regarded as:

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

It was assumed that partly/or fully the decomplexed IDA was mineralized to its end products, which was analyzed by its total organic carbon values. Moreover, the term of self-decomposition of ferrate(VI) which was pronounced even at higher pH values [34,42] was excluded since the necessary correction was done using the blank data at that pH and at an identical physical condition. The rate of decomposition of ferrate(VI) could be expressed as:

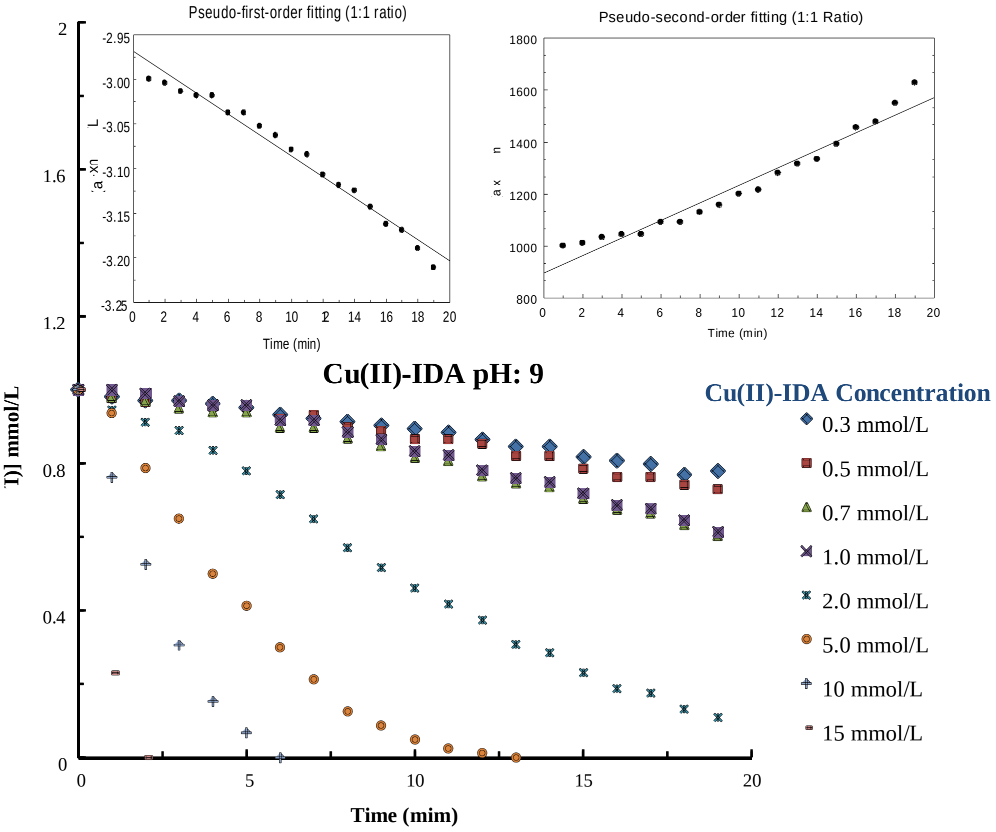

Fig. 1. Degradation of Fe(VI) as a function of time for various concentrations of Cu(II)-IDA at pH 9.0.

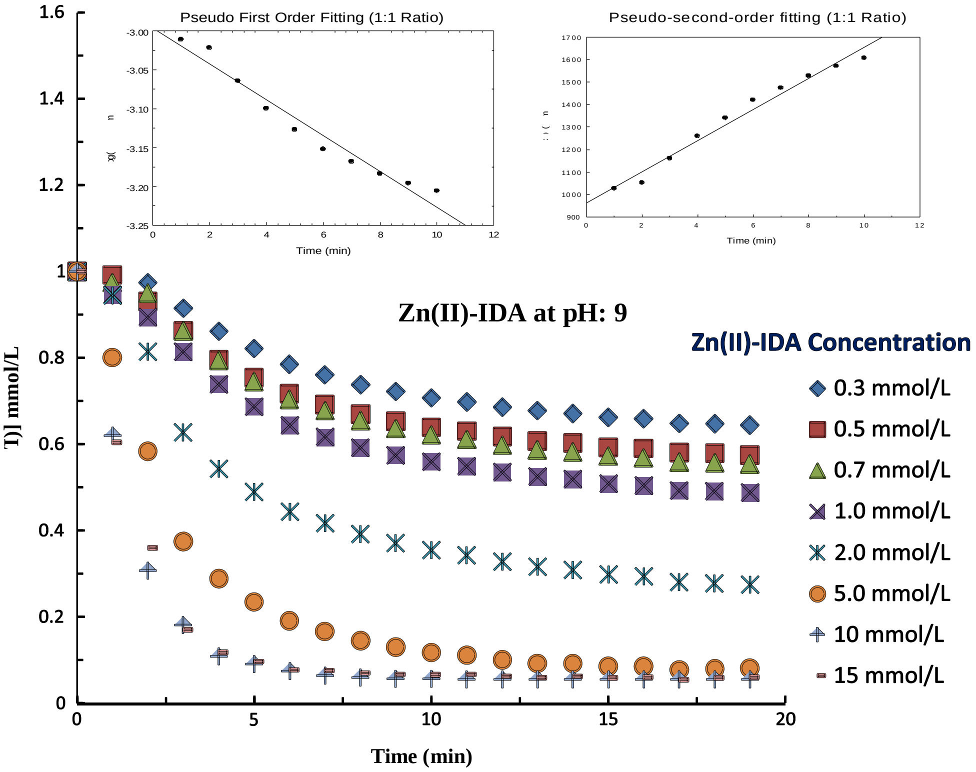

Fig. 2. Degradation of Fe(VI) as a function of time for various concentrations of Zn(II)-IDA at pH 9.0.

d½FeðVIÞ / dt ¼ k½FeðVIÞ$^{m}_{_}$½MðIIÞ _ IDA$^{n}_{_}$ ð6Þ

Or

d½FeðVIÞ / dt ¼ k$_1$½FeðVIÞ$^{m}_{\_}$ ð7Þ

where k$_1$ ¼ k½MðIIÞ _ IDA$^{n}_{\_}$ ð8Þ

[Fe(VI)] and [M(II)-IDA] is the concentration of ferrate(VI) and Cu(II)-IDA or Zn(II)-IDA in solution, respectively. ‘ k’ is the overall rate constant to each reactants, i.e., Fe(VI) and M(II)-IDA. ‘ m’ and ‘n’ are the order of reaction foreach species which was estimated with the empirical fitting of change in ferrate(VI) concentration and M(II)-IDA concentration data. In order to optimize the value of ‘ m’ the data was plotted between the Log(a _ x) vs ‘t’ and 1/(a _ x) vs ‘t’ as to demonstrate the pseudo-first order and pseudo-second order rate kinetics. The term (a _ x) is the concentration of Fe(VI) remained at time ‘ t’. The fitting results of pseudo-first and pseudo-second order equations were represented in Figs. 1 and 2 (inset in the figures) respectively for Cu(II)-IDA and Zn(II)-IDA systems at pH 9.0 having the 1:1M ratio of [Fe(VI)]/[M(II)-IDA]. The data was computed for all the studied molar ratios, i.e., 1:0.3–1:15 of [Fe(VI)]/[M(II)-IDA] and at different pH values, i.e., pH 8.0 to 12.0. The results were then returned in Tables 1 and 2 respectively for Cu(II)-IDA and Zn(II)-IDA systems. These results clearly inferred that decreasing the pH from 11.0 to 8.0, apparently, the rate of Fe(VI) reduction was increased significantly. Quantitatively, decreasing the pH from 11.0 to 8.0 the rate constant was increased, respectively from 0.39 _ 10^{-2} to 3.43 _ 10^{-2} min^{-1} (for pseudo-first-order) and from 4.05 to 48.09L/mol/min (for pseudo-second-order) obtained for Cu(II)-IDA at the 1:1M ratios of [Fe(VI)]/[Cu(II)-IDA]. Similar increase was observed for the Zn(II)-IDA system as decreasing the pH from 10.0 to 8.0 the increase in pseudo-first-order rate constant was from 5.09 _ 10^{-2} to 75.08 _ 10^{-2} min^{-1}, respectively whereas for the pseudo-second-order rate constant, it was increased from the 44.68 to 199.62 L/mol/min, respectively. The rapid and fast decomposition of ferrate(VI) at lower pH was, perhaps, due to the higher redox potential of Fe(VI) at lower pH values [24,25]. It was also noted that, apparently, at pH values 12.0 for Cu(II)-IDA system or even at pH 11.0 and 12.0 for Zn(II)-IDA system the rate of decomposition of Fe(VI) was almost independent with increasing the M(II)-IDA concentration (data not included). Moreover, the decomposition rate constant was also found to be significantly low values. This could be explicable with the fact that at very high pH conditions the reactivity of Fe(VI) was decreased greatly; whereas the stability of Fe(VI) was increased significantly at this high pH values which restricted the reactivity of Fe(VI) toward the oxidative reduction [23–25].

Further, using these rate constant values the overall rate constant ‘ k’ was estimated using the k$_1$ values (obtained by pseudo-first-order rate constant values as well the pseudo-second-order rate constant). It was observed that the value of ‘ n’ which was estimated for 1 and 2; best fitted for n =1; since the data was fitted fairly well to the pseudo-first-order rate constant values (cf Fig. 3) while plotting the line between various concentrations of M(II)-IDA vs k$_1$. Therefore, using the pseudo-first-order rate constant values, the overall rate constant values along with the R^2 values were estimated at different pH values and returned in Table 3 for these two systems. In general increasing the pH from 8.0 to 11.0 for Cu(II)-IDA and from 8.0 to 10.0 for Zn(II)-IDA, the overall rate constant values, i.e., k was decreased. This was in accordance to the reactivity of the ferrate(VI) in solution since the protonated ferrate species (HFeO$_4^-$ $ H^þ þ FeO$_4^2$; pKa^2=7.3) possessed with larger spin density than the deprotonated species [46,47]. These studies, clearly inferred that 1:1 stoichiometry was occurred in the decomplexation/degradation of M(II)-IDA by ferrate(VI).

3.2. Mineralization of IDA

The degradation of M(II)-IDA complex by ferrate(VI) was supposed to take place in two steps, i.e., in the first step the

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

[Cu(II)-IDA] (mmol/L)	Pseudo-first-order rate constant (_ 10^{-2}) (1/min)								Pseudo-second-order rate constant (L/mol min)							
	pH 8.0		pH 9.0		pH 10.0		pH 11.0		pH 8.0		pH 9.0		pH 10.0		pH 11.0	
	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
0.3	2.85	0.993	1.38	0.979	0.53	0.841	0.53	0.888	38.01	0.997	15.86	0.971	3.98	0.768	5.58	0.880
0.5	2.39	0.981	1.70	0.972	0.94	0.947	0.48	0.884	29.70	0.991	19.93	0.962	10.06	0.939	5.14	0.877
0.7	5.23	0.996	2.69	0.976	1.77	0.959	0.41	0.907	87.36	0.994	34.51	0.955	20.26	0.943	4.18	0.903
1.0	3.43	0.991	2.69	0.976	2.00	0.983	0.39	0.928	48.09	0.996	33.80	0.955	23.49	0.972	4.05	0.924
2.0	7.58	0.980	11.98	0.965	2.00	0.983	0.46	0.949	135.02	0.994	146.96	0.932	23.49	0.972	4.81	0.946
5.0	15.57	0.978	38.16	0.952	11.60	0.997	0.76	0.977	179.74	0.986	344.53	0.974	357.90	0.922	8.50	0.980
10.0	12.92	0.877	60.78	0.980	14.76	0.914	8.11	0.999	260.97	0.932	1710.80	0.887	1131.80	0.953	182.30	0.965
15.0	24.92	0.937	–	–	36.29	0.891	12.51	0.833	424.05	0.976	–	–	1880.00	0.970	852.20	0.982

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

[Zn(II)-IDA] (mmol/L)	Pseudo-first-order rate constant (_ 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	4.12	0.888	5.02	0.983	2.28	0.968	69.36	0.949	31.50	0.924	22.86	0.968
0.5	5.74	0.899	6.33	0.979	2.88	0.949	189.95	0.971	40.09	0.909	30.94	0.955
0.7	65.87	0.902	6.73	0.978	3.82	0.958	252.18	0.978	44.39	0.915	38.10	0.959
1.0	75.08	0.896	8.04	0.982	5.09	0.968	199.62	0.979	56.51	0.926	44.68	0.955
2.0	183.55	0.932	12.64	0.945	7.42	0.971	413.90	0.971	138.84	0.955	82.15	0.977
5.0	495.37	0.951	263.92	0.969	13.24	0.987	842.37	0.912	678.60	0.974	189.38	0.997
10.0	–	–	564.46	0.996	17.11	0.991	–	–	2053.80	0.982	311.54	0.998
15.0	–	–	554.10	0.992	–	–	–	–	1917.00	0.929	–	–

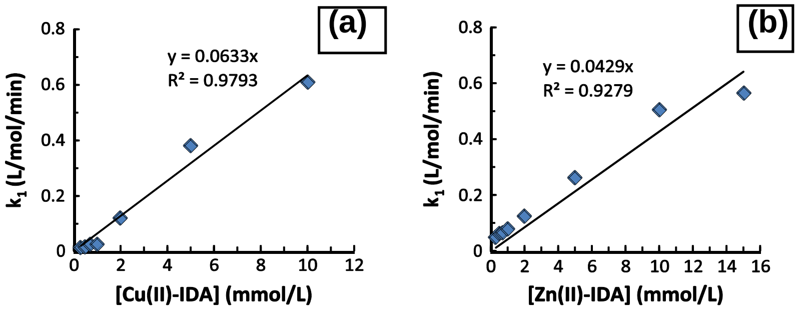

Fig. 3. Fitting of pseudo-first-order rate constant values with different concentrations of (a) Cu(II)-IDA; and (b) Zn(II)-IDA.

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

pH	Cu(II)-IDA system		Zn(II)-IDA system	
	k (L/mol/min)	R^2	k (L/mol/min)	R^2
8.0	32.30	0.950	97.42	0.993
9.0	63.00	0.979	42.91	0.928
10.0	16.30	0.919	29.49	0.806
11.0	7.70	0.922	–	–

decomplexation was taken place and in the next step the free IDA was oxidized and likely to be mineralized fully or partly. Therefore, the mineralization of IDA in the Fe(VI) treated samples of M(II)-IDA was conducted. The TOC values were then converted into the percent decrease in TOC using the initial TOC values. The percent decrease in TOC was represented in Fig. 4a and b, respectively for the Cu(II)-IDA and Zn(II)-IDA systems. The results were also compared with the single system, i.e., IDA only (cf Fig. 4c). Percent TOC removal was obtained for varied stoichiometric ratios, i.e., [Fe(VI)]/[M(II)-IDA] from 1:0.3 to 1:15 treated at different pH conditions, i.e., pH 8.0 to 12.0. These results indicated that higher percent of IDA was degraded at lower concentrations of IDA at a constant dose of Fe(VI). Decreasing the concentration of Cu(II)-IDA from 15.0 to 0.30 mmol/L the corresponding increase in percent removal of TOC was found to be from 1.91% to 46.68% at pH 8.0. Similarly, for the Zn(II)-IDA system, the corresponding increase in TOC percent removal was recorded from 15.41% to 52.14%, respectively at pH 8.0. On the other hand, the IDA was mineralized from 3.25% to 98.02%, respectively, decreasing the concentration of IDA from 15.0 to 0.3 mol/L at pH 8.0. These results were in a line that more and more percent of IDA was degraded at lower IDA concentrations at a constant dose of Fe(VI). Further, it was again reaffirmed that lower pH values, i.e., at pH 8.0 favored greatly the degradation of IDA in solution. These results were in accordance to the previous studies conducted for the degradation of trichloroethylene by Fe(VI) in which it was degraded maximum at pH 8.0 and decreased further up to pH 11.0 [48].

3.3. Simultaneous removal of metal ions

An additional advantage of the ferrate(VI) treatment was a simultaneous removal of non-degradable metallic impurities by the coagulation/flocculation or even by the adsorption pathways

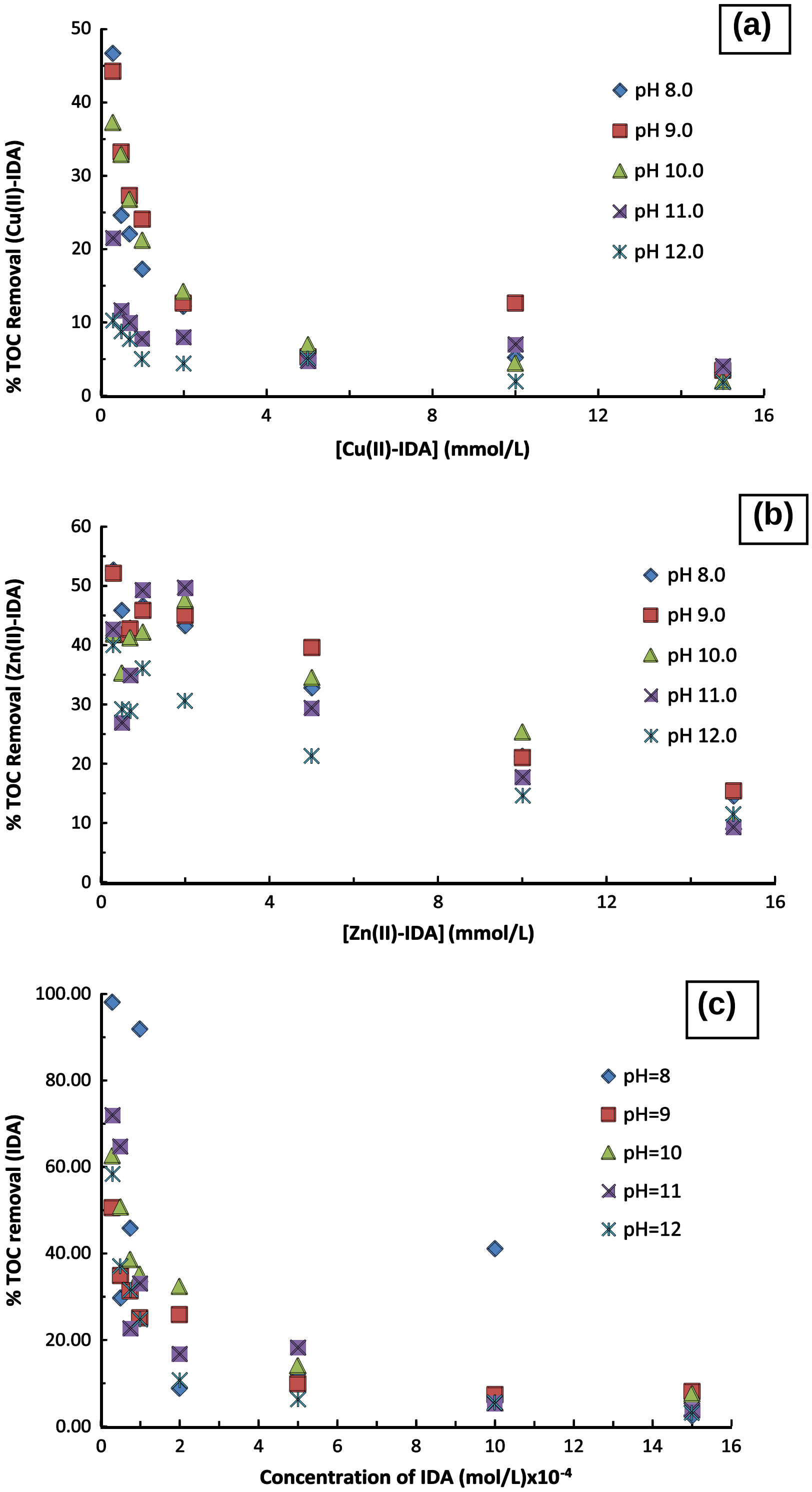

Fig.4. MineralizationofIDAinthesampleof(a)Cu(II)-IDA;(b)Zn(II)-IDA;and(c)IDAfordifferentconcentrationsofIDAtreatedwithFe(VI):1.0mmol/L(1.0 _ 10^{-4} mol/L forIDA)atdifferentpHvalues.

occurredwiththereducedferrateintoFe(III).TheFe(III)wasnoted reasonably an excellent coagulant [43,48]. Hence, the study was further extended for the simultaneous removal of Cu(II) or Zn(II) from the Fe(VI) treated samples. The removal of M(II) was obtained; analyzing the treated and filtered samples at the treated pHaswellatthehigherpH,i.e.,atpH12.0byraisingthesolution pH12.0 bydropwiseadditionofconc.NaOHsolution.Thesimultaneous Cu(II) and Zn(II) removal was presented graphically in Figs.5and6,respectivelyforCu(II)andZn(II).These3Dfiguresobtainedforvariousconcentrationsof M(II)-IDAshowedthat partial butinsignificantremovalofthesemetalionswereoccurredatthe lower pH values however, very high percent removal of Cu(II) or Zn(II) were occurred when the treated sample pH was raised to pH 12.0. Quantitatively, at pH 8.0 the percent of Cu(II) was removed only 1.10% at 1:1 [Fe(VI)]/[Cu(II)-IDA(II)] ratio. However, it was increased by 90.68% raising the solution pH 12.0. On the

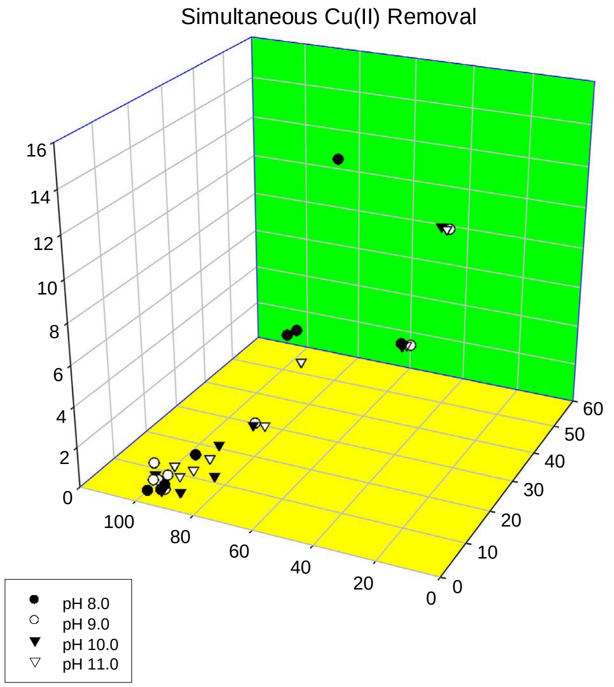

Fig. 5. Simultaneous removal of Cu(II) for different concentrations of Cu(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH values.

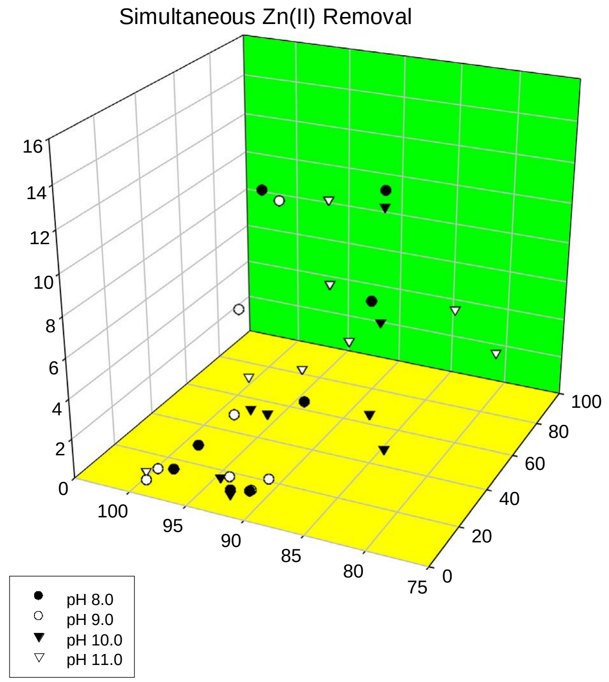

Fig. 6. Simultaneous removal of Zn(II) for different concentrations of Zn(II)-IDA treated with Fe(VI): 1.0 mmol/L at different pH values.

other hand, the percent removal of Zn(II) was only 5.06% and was increased by 90.25% at 1:1 [Fe(VI)]/[Cu(II)-IDA(II)] ratio These results clearly indicated that the M(II)-IDA species treated at various pH values were decomplexed completely and the mineralization of IDA was occurred partly. However, the decomplexed Cu(II) or Zn(II) was coagulated significantly at higher pH values since more than 90% of Cu(II) or Zn(II) was removed at pH 12.0. Previous studies, also indicated that a significant percent of Cu(II) or Ni(II) was removed simultaneously as treated by Fe(VI) at different pH values [30]. Moreover, the Cu(I)-cyanide was treated with Fe(VI) and with increasing the dose of Fe(VI) enables to remove completely the Cu(II) simultaneously by reduced Fe(III) [32]. An enhanced removal of heavy metals was achieved by the coagulation/flocculation process using the ferric chloride dose in the primary treatment of wastewaters [49–51].

4. Conclusions

Ferrate(VI) was employed in the treatment of wastewater contaminated with the Cu(II)-IDA and Zn(II)-IDA complexed species under the batch reactor operations. A fast and effective decomplexation/degradation of metal(II)-IDA complexed species was occurred under the various pH values (pH 8.0–12.0) and at different M(II)-IDA concentrations (i.e., 0.3–15.0 mmol/L). Increase in concentration of M(II)-IDA caused an apparent increase in Fe(VI) reduction. Moreover, the kinetic studies inferred a 1:1 stoichiometry was obtained for each reactant in the oxidation of M(II)-IDA by Fe(VI). Moreover, the overall rate constant values were decreased increasing the pH values from 8.0 to 11.0 for Cu(II)-IDA system and from pH 8.0 to 10.0 for Zn(II)-IDA system. The mineralization of IDA was obtained with %TOC removal, which indicated that a significant percent of IDA was mineralized with Fe(VI) treatment. The percent removal of TOC was decreased with increasing the concentration of M(II)-IDA. However, the maximum TOC was removed at pH 8.0. On the other hand the simultaneous removal of Cu(II) and Zn(II) was obtained by simple filtration and showed that insignificant removal of metals was obtained through coagulation/flocculation process which was greatly enhanced, raising the treated sample pH to 12.0. The comprehensive study showed a potential use of ferrate(VI) in the effective and efficient treatment of M(II)-IDA contaminated wastewaters. Moreover, since the treatment is devoid of any toxic by-product hence, to be known as ‘environment benign’ treatment process.

Acknowledgement

One of the authors D.T. wishes to acknowledge the Department of Science & Technology, New Delhi for the financial support; received in the form of Project vide No.:SR/S1/IC-35/2010.

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