FENTON AND PHOTOFENTON OXIDATION OF ANILINE DERIVATIVES IN WATER

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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D E C L A R A T I O N

I hereby *declare* that the Research Thesis entitled **Fenton and Photo-Fenton Oxidation of Aniline Derivatives in Water** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Department of Civil Engineering** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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C E R T I F I C A T E

This is to *certify* that the Research Thesis entitled **Fenton and Photo-Fenton Oxidation of Aniline Derivatives in Water**, submitted by **Amritha A. S.** (Register Number: **121169CV12P04**) as the record of the research work carried out by her is *accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy**.

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ABSTRACT

Aniline derivatives are dye intermediates with wide applications. Disposal of untreated effluent containing these derivatives is detrimental to the receiving water bodies. Hence, new and improved treatment methods are being investigated to effectively degrade and remove these harmful compounds from industrial effluents before disposal. In the present study, oxidation of some of the selected aniline derivatives viz. 2-Nitroaniline (2-NA), 3-Nitroanailine (3-NA), 4-Nitroaniline (4-NA), 2-Methoxyanailine (2-MA) and 4-Methoxyanailine (4-MA) using Fenton and photo-Fenton oxidation methods were carried out. Fenton's and Photo-Fenton oxidation process seems to be a simple and cost-effective method for degradation of organic compounds in effluents. However, iron is found to increase the cost of treatment. Hence, iron extracted from the laterite soil (LS) was evaluated as a catalyst in the above treatment techniques. Optimization of pH, hydrogen peroxide concentration and iron concentration was carried out for different initial concentrations of 2-NA, 3-NA, 4-NA, 2-MA and 4-MA in water using $FeSO_4$ and iron extracted from laterite (LS) as a catalyst. The optimum pH obtained was 2.5 & 3 for the selected compounds. The optimum hydrogen peroxide concentration obtained was in the range of 3.5 mM – 5 mM and iron concentration of 0.05 mM for the maximum removal efficiencies at 0.5 mM of initial concentration. The corresponding Hydrogen Peroxide/Iron (H/F) ratio was in the range of 70-108 for Fenton's oxidation process for the varied initial concentration of aniline derivatives in the range of 0.5 mM - 2.5 mM. The removal efficiency observed was 4-NA>2-NA>3-NA and 4-MA>2-MA. Removal efficiencies obtained for Photo-Fenton oxidation were 4-6% higher than the Fenton process. Kinetic studies were carried out for the initial concentration of 0.5 mM for both Fenton & Photo-Fenton oxidation processes using $FeSO_4$ and iron extracted from laterite as sources of iron. It was found that kinetic rate constant was higher for Photo-Fenton oxidation process compare to the Fenton oxidation process. During Fenton and Photo-Fenton studies for a mixture of aniline derivatives, maximum removal efficiencies obtained were 92.3%, 86.2%, 94.7%, 98.1% and 89.7% respectively for 2-NA, 3-NA, 4-NA, 2-MA & 4-MA. Maximum removal efficiency was obtained for Photo-Fenton technique using $FeSO_4$.

Keywords: Aniline, Fenton's oxidation, H/F ratio, Laterite soil, Photo-Fenton oxidation

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CHAPTER 1

INTRODUCTION

Water is a basic necessity to sustain life. The major uses of water include agricultural, industrial, household, recreational and environmental activities. In India, agriculture is the highest consumer of water, followed by industries. In the recent years, industrial development has resulted in increased water demand. The consumption of water depends on the type of industry. Thermal power, pulp and paper, textiles and iron and steel are highly water intensive sectors; whereas, industrial sectors like chlor-alkali, copper and zinc, cement and plastics require little water. Data on actual water consumption in India is not readily accountable since the industries consume water from different sources such as surface water, ground water or water supplied in tankers by the municipality. The choice of source of water depends on the availability of sufficient and regular supply of water and the cost of water from the source. However, the data on wastewater discharge by various industrial sectors in the country is available, which has been compiled by CPCB (Aggarwal and Kumar, 2011). A large part of the water consumed by the industries is discharged as wastewater. Polluted water is very rarely treated and reused by industries. The future demand will inevitably put pressure on the available freshwater resources, both due to water consumption and wastewater generation.

In order to overcome water shortage, an integrated approach is required, which focuses both on water conservation and on wastewater recycling. Water conservation reduces water wastage at the source, while recycling and reuse of wastewater promotes reclaiming of used water. In this approach, wastewater is considered as an alternative source of raw water. Recycled water is less expensive, in terms of capital and operational cost, when compared to the cost of water in the long run, particularly for industries where the cost of water is higher; typically, 40-70 rupees per 1,000 litres.

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1.1 BACKGROUND AND MOTIVATION

Environmental pollution caused due to industrial wastewater is a major concern. Disposal of untreated wastes and effluents in the environment affect both soil and water quality. Careless disposal of carcinogenic wastes into receiving water sources will lead to a number of health problems and adversely affect the quality of life on earth. Untreated effluents from industries such as dyes, pharmaceuticals, pesticides, antiseptic agents, medicines for pharmaceutical and poultry synthesis, gums, distillery, dye intermediates and printing are the larger contributors that deteriorate the water quality. These industries use more than ten thousand commercial products and chemicals such as aniline and its derivatives, chemical dyes, surfactants, chelating agents, pH regulators, densifiers, etc.

Aniline derivatives are widely used in the manufacture of dyes, intermediates for antioxidants, gum inhibitors, corrosion inhibitors, intermediate for pharmaceutical and gasoline and poultry medicine. The unused and unwanted aniline derivatives have a dangerous health effect on humans and also on aquatic life. The toxicity of the aniline compounds is very high even in low concentration and may lead to irreversible damage.

The acute health effects of aniline derivatives may be caused due to accidental ingestion or direct contact. Contact with eyes may result in transient discomfort characterized by tearing or conjunctive redness. Skin contact with the compound may produce toxic effects. Inhalation of vapours or aerosols (mists, fumes) generated by the compound during the course of normal handling, may produce toxic effects. Light headedness, increasingly severe headache, ataxia, rapid shallow respiration, drowsiness, nausea, vomiting, confusion, lethargy and stupor etc. are some of the other health effects of the aniline derivatives. Long-term occupational exposure may result in the chronic health effects such as pneumoconiosis. High chronic doses may cause congestion of the spleen and tumour formation and prolonged exposure may produce liver damage.

Aniline derivatives are recalcitrant and hence remain in water and soil for a long period of time, causing detrimental impacts on environmental quality. Therefore, it is important to treat the wastewater containing these compounds before discharging

into water bodies (Jiang et al., 2016). New and improved treatment methods are being researched to effectively degrade and remove these harmful compounds present in the industrial effluents before disposal into the environment.

The treatment of aniline derivatives contaminated wastewater is a great challenge encountered by the researchers across the world at present. Existing literature highlights the deployment of biological, chemical and physical methods for the removal of these compounds. It is reported that aniline derivatives are not easily degraded and also inhibit the biodegradation of other chemicals (Liu et al., 2012). This may be due to the nitro group present in the aromatic ring which enhances the stability of the compound. Biological treatment, although economical, is thus less efficient in the removal of aniline derivative compounds and hence, other treatments are necessary for these toxic compounds. The physical methods may not remove the aniline derivatives completely and are uneconomical as well. Among the chemical treatment methods, the advanced oxidation processes (AOPs) appear to be promising treatment method to remove the aniline derivatives (Sun et al., 2008). The advanced oxidation processes are based on the generation of hydroxyl radical, which is a powerful oxidizing agent. The complex organic compounds are oxidized to carbon dioxide and water (Wang et al. 2016).

Among the AOPs for water contaminated by organic compounds, application of Fenton's reagent (a result of the reaction between hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) that produces hydroxyl radicals) is one of the most promising techniques (Sun et al., 2007). Fenton's oxidation process has gained a lot of attention due to its advantages of low capital cost, high efficiency and easy operation and maintenance. The iron species catalyze the decomposition of H_2O_2 to produce free radicals including hydroxyl free radical ($OH^\cdot$). The hydroxyl radical is a powerful, non-selective chemical oxidant, which acts very rapidly with most organic compounds. Once generated, the hydroxyl radicals aggressively attack virtually all organic contaminants, including PAHs, phenols, dyes, pesticides, etc. These produced free radicals have a strong non-selective oxidizing ability and can degrade aniline easily in an aqueous system. Fenton's reaction requires strong acidic environment (pH = 2 to 4), which significantly limits its application (Liu et al., 2016). Besides, the high

cost of hydrogen peroxide is a major disadvantage, notwithstanding a large amount of ferric sludge produced during the Fenton process which causes other environmental problems. To overcome these disadvantages of classic Fenton's oxidation process, various alternatives have to be considered to ensure economical as well as efficient degradation of persistent organic contaminants.

Photo-Fenton oxidation is a promising and attractive alternative treatment method to overcome the limitations of Fenton's process. The additional advantage of UV light in the Photo-Fenton oxidation apart from the increase in the formation of hydroxyl radicals, is the recycling of ferrous catalyst by the reduction of ferric ions (Fe3+). This increases the net concentration of ferrous ion, thereby accelerating the overall reaction. The implementation of Photo-Fenton oxidation for in situ and small scale treatment plants is easy because of the advantages like, high efficiency in oxidizing a variety of organic compounds, simplicity of operation and possibility of using solar light as an alternative source for UV light (Fonseca et al., 2010).

AOPs like the Fenton's and photo-Fenton's process play an important role either by enhancing the wastewater treatment in order to achieve the desirable limits for discharge of treated wastewater into natural water bodies, or to minimize the effluent toxicity and enhance its biodegradability to promote an efficient post biological treatment in municipal wastewater treatment plant (Martins et al., 2010).

There is also a need to develop an economical process for the removal of the hazardous chemicals from wastewater contaminated with industrial effluent using a low cost naturally available material such as laterite which, as a catalyst, can enhance the availability of hydroxyl radical.

1.2 OBJECTIVE

To develop a cost effective method for removal of selected aniline derivatives in water viz Anisidine and Nitroaniline.

1.2.1 Specific objectives

- To evaluate the effect of pH, Fe^{2+}, H_2O_2, and initial concentration on the degradation of aniline derivatives.

- To evaluate the effect of iron extracted from laterite soil on the degradation of aniline derivatives.

- Kinetic studies on the degradation of aniline derivatives at the optimum conditions.

- To evaluate the effect of pH, Fe^{2+}, H_2O_2, and initial concentration on the degradation of a mixture of aniline derivatives.

1.3 ORGANIZATION OF THESIS

The dissertation has been divided into 4 chapters. **Chapter 1** briefly explains the area of research and also lists the objectives of the present research work. **Chapter 2** presents a comprehensive literature review about aniline derivatives in wastewater, their occurrence and health effects, as well as, treatment options available for their removal from wastewater. This chapter also includes a summary of the review of the literature and the identified gaps in the review. **Chapter 3** provides the details of various materials used and experimental methodology adopted for achieving the specific objectives of this study. **Chapter 4** discusses the results obtained in this study, summarizes those results and presents the conclusions thence derived. The **Appendix** contains the UV-VIS spectrums, calibration curves and also HPLC chromatographs of aniline derivatives obtained during the course of this study.

CHAPTER 2

LITERATURE REVIEW

Water is one of the most vital natural resources for all life on Earth. The availability and quality of water always plays an important part in determining not only where people can live, but also their quality of life. The balance between supply and demand for water is a delicate one. Inefficient consumption of freshwater exerts a major pressure on the water resources. Agriculture is the highest consumer of water in India, closely followed by the industries. In the recent years, industrial development has resulted in increased water demand. Some of the water intensive industries have grown quite substantially, further increasing the industrial demand for water. There is no readily available data for industrial water consumption in India. Agencies report different estimates of water consumed by the industries. For example, according to the CWC, Ministry of Water Resources (2010), the industrial water demand constituted about eight percent of the total water demand in 2010. However, the World Bank estimates that the current water consumption by the industries in India is about 13 percent of the total freshwater abstraction in the country. The water demand for industrial uses and energy production will continue to grow at a rate of 4.2 percent per year, rising from 67 billion cubic metres in 1999 to 228 billion cubic metres by 2025 (Aggarwal and Kumar, 2011).

Industries not only consume a large quantity of water but also contaminate it. A large part of the water consumed by industries is discharged as wastewater. In most cases, industrial wastewater is discharged without necessary treatment, thereby polluting the available natural water supply. On an average, each litre of wastewater discharged further pollutes about 5 to 8 litres of fresh water which increases the actual share of industrial water consumption to about 35 to 50 percent of the total water used in the country and not the 7 to 8 percent that is reported as the industrial water use. Polluted water is rarely treated and reused by the industries. Water use and wastewater disposal are on the rise due to the lack of clear environmental policies as well as fragmented responsibility and control over water used for industrial purposes (CSE 2004). The future demand will definitely increase the pressure on the available

freshwater resources, both due to water consumption and wastewater generation. Table 2.1 provides the estimates of water consumption and wastewater generated by different industries in India.

Table 2.1 Wastewater Generation and Water Use by different Industries in India, 2004 (CSE 2004)

Industrial Sector	Annual wastewater discharge (million cubic metres)	Annual consumption (million cubic metres)	Proportion of total water consumed by industry (percent)
Thermal power plants	27,000.9	35,157.4	87.87
Engineering	1551.3	2019.9	5.05
Pulp and Paper	695.7	905.8	2.26
Textiles	637.3	829.8	2.07
Steel	396.8	516.6	1.29
Sugar	149.7	194.9	0.49
Fertilizers	56.4	73.5	0.18
Others	241.3	314.2	0.78
Total	**30,729.2**	**40,012.0**	**100**

Dye manufacturing industries, pharmaceutical industries, pesticides etc., represent the strong and fast going sector of the Indian industries. More than 100,000 commercially available textile dyes are present in the market. It is found that textile industries produce approximately 7,00,000 to 10,00,000 tons of dyes annually, out of which, 2,80,000 tons are discharged to the global environment via effluents generated (Christie, 2007). The textile industry has one of the most significant contributions to the production of large volumes of highly polluted and toxic wastewater. The World Bank estimates that 17 – 20 % of industrial water pollution is contributed by the

textile industry. Treating this wastewater and discharging into receiving water bodies could cost over billion dollars every year. The effluent from textile industries has a complex composition due to the variation in raw materials and manufacturing techniques. Textile wastewater is often rich in colour and also of extreme pH with various types of chemicals (persistent and toxic) (Jegatheesan et al., 2016).

Industries like dyes, pharmaceuticals, pesticides, antiseptic agents, medicines for pharmaceutical and poultry synthesis, gums, distillery, dye intermediates and printing use more than ten thousand commercial products and chemicals such as aniline and its derivatives, chemical dyes, surfactants, chelating agents, pH regulators, densifiers, etc. Aniline derivatives are dye intermediates with wide applications and some of the most extensively used derivatives are 2-nitroaniline, 3-nitroaniline and 4-nitroaniline (Sun et al., 2007). They are used in different type of dyes such as direct dyes, acetate dyes and disperse dyes. All these three dyes are produced in China, yet only direct dye is produced both in China and India. The average production of 4-NA in India is 550 metric tons per month and 4000 tons per month for China (Gautam et al., 2005). China is the major exporter of 4-NA whereas India is the major importer.

With growing number of industries, concern towards the rapidly rising volume of the wastewater generation has also tremendously increased. Moreover, some industries cannot install and effectively operate wastewater treatment plant, due to lack of space, technical manpower, and often finances, which constraints their ability to control pollution. The disposal of untreated effluents containing these derivatives is detrimental to the receiving water bodies and new and improved treatment methods are being researched to effectively degrade and remove these harmful compounds present in the industrial effluents before disposal into the environment. To address this wastewater disposal from industries, adoption of cleaner production technologies and waste minimization initiatives are being encouraged across the world. Industrial wastewater, depending on its characteristics, is subjected to different treatment methods. Conventional wastewater treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic matter and, sometimes, nutrients from wastewater (Hangargekar and Takpere, 2015).

The conventional biological treatment methods are not very efficient in removing these compounds although economical. The physical methods may not remove the aniline derivatives completely and are uneconomical as well. Among the chemical treatment methods, the advanced oxidation processes (AOPs) appear to be promising treatment method to remove the aniline derivatives (Sun et al., 2008). The advanced oxidation processes are based on the generation of hydroxyl radical, which is a powerful oxidizing agent.

2.1 ANILINE DERIVATIVES IN WASTEWATER

Aniline and its derivatives can be introduced into the environment through a number of sources. Chloro, nitro and dimethylanilines (xylidines) are widely used as intermediates for the synthesis of chemicals in the pharmaceutical, agrochemical and pigment industries and can be released into the environment through industrial discharge. Halogenated anilines can form as a result of the partial degradation of certain aniline based pesticides. These compounds are known to cause a variety of toxic effects, whose magnitude and type depend on the nature of the substituent groups, on their number and in addition, on their position in the aromatic ring. Various studies demonstrated that aniline and halogenated anilines can induce methaemoglobineaemia, as well as renal and hepatic toxicity both in vitro and in vivo (Argese et al., 2002).

The reactivity of benzene ring in aniline depends on the type of substituent atoms or groups of atoms. If an atom or group makes the ring more reactive, it is called activating and if less, then it is called deactivating (http://en.wikibooks.org/wiki/Organic_Chemistry/Aromatics). Table 2.2 shows some of the substituents of activating and deactivating groups.

Table 2.2: Activating and Deactivating substituent groups

Type	Group	Strength	Directing
Activating substituent groups	$-NH_2$, $-NHR$, $-NRR$	very strong	ortho/para
	$-OH$, $-O^-$	very strong	ortho/para
	$-NHCOCH_3$, $-NHCOR$	strong	ortho/para
	$-OCH_3$, $-OR$	strong	ortho/para
	$-CH_3$, $-C_2H_5$, $-R$	weak	ortho/para
	$-C_6H_5$	very weak	ortho/para
Deactivating substituent groups	$-NR_3^+$	very strong	meta
	$-NO_2$	very strong	meta
	$-CF_3$, CCl_3	very strong	meta
	$-CN$	strong	meta
	$-SO_3H$	strong	meta
	$-CO_2H$, $-CO_2R$	strong	meta
	$-COH$, $-COR$	strong	meta
	$-F$	weak	ortho/para
	$-Cl$	weak	ortho/para
	$-Br$	weak	ortho/para

The nitro group (NO_2) is deactivating whereas methoxy group (OCH_3) is an activating group, which makes the degradation of aromatic compounds containing methoxy group easier than those containing the nitro group.

2.1.1 Sources, occurrence and fate of aniline derivatives

The release of aniline derivatives directly through production or utilization process causes many serious eco-environmental problems due to the toxicity, carcinogenic and mutagenic effects (Sun et al., 2007). A liquid effluent is released to the environment only after physico-chemical, biological treatment.

2.1.2 Acute health effects

The toxicity of aniline derivatives is very high even in low concentration and hence leads to maximum damage. The LD_{50} values of 2-NA for rat and mouse are 1838 mg/kg and 1290 mg/kg respectively whereas the LD_{50} values of 3-NA for rat and mouse are 900 mg/kg and 310 mg/kg. The LD_{50} values of 4-NA for rat, pig, mouse are 750 mg/kg, 450 mg/kg and 810 mg/kg respectively (http://www.inchem.org/documents/sids/sids/NITROANILINE.pdf). The LD_{50} of 2-MA for rabbit and rat are 870 mg/kg and 1150 mg/kg respectively whereas, in the case of 4-MA, the LD_{50} values for rabbit and rat are 2900 mg/kg, 1320 mg/kg respectively. Nitro-aromatic compounds are, on the average, over 500-fold more toxic than their corresponding aromatic amines (Donlon et al., 1995).

Ingestion: Accidental ingestion of the compound may result in toxic effects. Animal experiments indicate that ingestion of less than 40 gram may be fatal or may produce serious damage to the health.

Nitroaniline and its metabolites may bind to haemoglobin inhibiting normal uptake of oxygen, resulting in a condition, known as "methemoglobinemia", which is a form of oxygen deficiency. Cyanosis and breathing difficulties are some of the symptoms. Symptoms may not be evident until several hours after exposure. Euphoria, flushed face and headache are commonly experienced in the absence of clear symptoms. At 25-40%, cyanosis is noticeable and at 40-60%, symptoms include weakness and dizziness.

Eye: Although nitroaniline is not considered to be an irritant, direct contact with the eye may cause short term discomfort redness of eyes.

Skin: Systemic effects may result during skin contact. Nitroaniline is not reported to be a skin irritant (as classified using animal models). However, prolonged exposures may result in abrasive damage. Open cuts, abraded or irritated skin should be prevented from exposure to nitroaniline. Entry into the blood-stream through cuts, abrasions or lesions, may produce systemic injury with harmful effects.

Inhalation: Inhalation of vapours or aerosols generated by the compound during the course of normal handling may produce toxic effects. Nitroaniline is not observed to produce respiratory irritation (as classified using animal models). Nevertheless, inhalation of dust, or fume, especially for prolonged periods, may produce respiratory discomfort and occasionally, distress. It may worsen the condition of people with impaired respiratory function, airway diseases if excessive concentrations of particulate are inhaled.

Other Health effects: Other health effects include ataxia, confusion, light headedness, rapid shallow respiration, drowsiness, nausea, vomiting, lethargy, severe headache and stupor. At concentrations above 60%, symptoms include tachycardia or bradycardia, convulsions and respiratory depression. Concentration levels exceeding 70% may be fatal.

2.1.3 Chronic health effects

Long-term occupational exposure to nitroaniline is likely to produce cumulative health effects like pneumoconiosis, caused by particles less than 0.5 microns penetrating and remaining in the lung. Prime symptom is breathlessness. Most arylamines are toxic to the blood-generation system. High doses cause congestion of the spleen and tumour formation. Prolonged exposure may produce liver damage in workers. Male mice showed an increased incidence of hemangiosarcoma or hemangioma when administered p-nitroaniline by intubation (30 or 100 mg/kg/day) (http://www.westliberty.edu/health-and-safety/files/2012/08/p-Nitroaniline.pdf).

2.2 TREATMENT TECHNOLOGIES ADOPTED FOR REMOVAL OF ANILINE DERIVATIVES FROM WASTEWATER

A number of physical, chemical and biological methods are available for the treating wastewaters containing aniline derivatives. Physical treatment methods consist of floatation, sedimentation, filtration, ion exchange, adsorption, stripping and other processes that remove soluble and insoluble substances without altering their chemical structure. Chemical methods include chemical precipitation, chemical oxidation or reduction including advanced oxidation processes (AOPs). Biological treatment processes are mainly used for secondary treatment of wastewater and are based on the microbial action to decompose suspended and dissolved organic compounds in the wastewater. These microbes use the organic compounds as both a source of carbon and as a source of energy.

2.2.1 Biological treatment methods

Biological processes are a good option for wastewater treatment as they are relatively economical and the end products of complete degradation are harmless.

In a study carried out by Saupe (1999), a municipal wastewater bio sludge was acclimated to the degradation of 4-nitroaniline (4-NA). This was achieved by using this compound as the sole source of nitrogen during the degradation of succinate as the sole source of carbon and energy. Bacteria were able to eliminate and mineralize 4-NA as the sole source of carbon and energy. The degradation process was found to be unstable and occurred at comparatively low rates in the batch studies. To overcome these drawbacks, a continuously operated miniaturized fixed-bed bioreactor was inoculated with the acclimated bacteria and fed with 4-NA as the sole substrate. After gradual adaptation, the bacteria also degraded 3-NA and 4-NA simultaneously in this system. Additional batch tests showed, that 3-NA can serve as the sole source of carbon, nitrogen and energy.

2.2.2 Chemical treatment methods

Treatment using chemical process can be used as an alternative when biological treatments do not completely remove the aniline derivatives from water and wastewater. Among the various chemical treatment methods, advanced oxidation processes (AOPs) are reported to be most effective in the removal of non-biodegradable substances.

Advanced oxidation processes have been studied as a promising kind of wastewater treatment system to treat the organic wastewater. Under advanced oxidation process, the complex organic molecules are either oxidized to smaller molecules or to the carbon dioxide and water (Wang et al., 2016).

The AOPs are defined as the near ambient temperature and pressure water and wastewater treatment processes, which involve the generation of highly reactive hydroxyl radicals. These hydroxyl radicals are extremely reactive species that attack most of the organic molecules.

AOPs can be classified as homogenous or heterogeneous processes. AOPs include Fenton type oxidation, ozonation, photo-catalysis, UV-H_2O_2, UV-H_2O_2-Fe (II, III), electro coagulation and electron decomposition that oxidizes the non-biodegradable organic compounds with the OH radical which are produced during reactions. AOPs are the promising alternatives for destroying toxic and bio refractory organic compounds.

4-Nitroaniline, a non-biodegradable contaminant is usually manufactured or used as an intermediate during the synthesis of pharmaceuticals, azo dyes and corrosion inhibitors. The chemical stability and toxicity of 4NA makes it hazardous once it enters the natural water bodies and it is considered toxic for human health and aquatic microorganisms even at significantly low concentrations. 4NA has been listed by the National Environmental Protection Agency (NEPA) of the People's Republic of China as one of the priority pollutants for removal from water (Zhao et al., 2015).

Many attempts have been made for the treatment of 4NA wastewater, including physical, chemical & biological methods. 4NA is resistant to biological degradation due to the presence of a nitro group in the aromatic ring which enhances

its stability. Hence the rate of degradation is quite low. The physical methods manage to transfer the contaminants from one medium to another such as activated carbon, in which the degradation or mineralization could be achieved. However, further treatment is required using chemical methods for decomposition of nitroaniline. Photo catalytic degradation is has a few drawbacks like high capital and operating cost. Hence, new cost-effective technologies have to be developed to treat 4NA-contaminated wastewater.

In the conventional AOPs, $FeSO_4$ & similar compounds are used as a catalyst to release the hydroxyl radical from peroxide and present research focus is towards finding low cost material containing iron to substitute the ferrous compound.

Ferric iron (III) can be extracted from laterite soil using sulphuric acid or HCl as leaching agents. Laterite often contains secondary oxides of iron, Aluminium or both, minor amounts of Nickel, Cobalt, Chromium, Quartz and Kaolinite, and is nearly devoid of basis and primary silicate. The high proportion of Iron (III) oxide in laterite represents a residual accumulation brought about by the removal of silica and alkali.

2.2.2.1 Fenton oxidation process

The Fenton reagent is a mixture of H_2O_2 and ferrous ion, which dissociates the oxidant (H_2O_2) and forms highly reactive hydroxyl radicals. The hydroxyl radical (OH·) is a powerful, non-selective chemical oxidant, which rapidly oxidizes most organic compounds. Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds (Parmar, 2014).

After addition of the iron and the hydrogen peroxide, they are going to react together to generate some hydroxyl radicals (Barbusinki et al., 2009) as it shown in the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{1}$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{2}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{3}$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \tag{4}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{5}$$

$$Fe^{3+} + OH^{\bullet} \rightarrow FeOH^{3+} \tag{6}$$
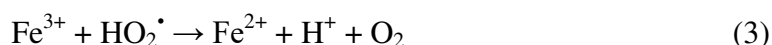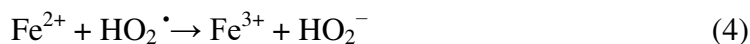
It is a chain reaction with step (1) serving as chain initiation, steps (4) and (5) as termination and the cycle (1)-(2)-(3) forms the chain which is the site of O_2 evolution. In the free radical mechanism, reaction (2) becomes insignificant at low $[H_2O_2]$ as a mode of reaction of $OH^{\bullet}$. Hydroxyl radical could then react with Fe^{2+} and produce Fe^{3+} (reaction (5)). As an alternative, $OH^{\bullet}$ could react with Fe^{3+} (reaction (6)). If this reaction occurred it would be even more plausible to assume that the pair Fe^{3+} + $OH^{\bullet}$ (as products of reaction 1) would not become separated at all and the species $FeOH^{3+}$ would appear instead. It can be stated that the species $FeOH^{3+}$ is merely the protonated form of FeO^{2+}.

Some of the advantages of Fenton oxidation process over the conventional treatment methods include:

- Highly effective at removing organic compounds that are resistant to conventional treatment methods

- Capable of complete mineralization of organic compound into carbon dioxide

- Less susceptible to the presence of toxic chemicals

- Produce less harmful by-products

- Low maintenance

- Rapid process

- Low production of residual sludge

- Excess H_2O_2 degrades to oxygen in the solution

One of the advantages of the Fenton process with respect to other advanced oxidation processes is that it does not require any energy input to activate hydrogen peroxide because the reaction takes place at atmospheric pressure and at room temperature. The main disadvantages are the high cost of chemicals (hydrogen

peroxide and iron) in addition to the cost of removal of homogeneous catalyst (iron salt) to prevent further pollution of water (Bautista et al., 2008).

2.2.2.2 Photo Fenton process

Photo-Fenton oxidation is a promising and attractive treatment method to overcome the drawbacks of Fenton's oxidation process. The rate of Fenton reaction is strongly enhanced by irradiation with UV or visible light. The photo-Fenton reactions involve irradiation with UV light or solar rays which significantly increase the rate of contaminant degradation by photo reduction of Fe^{3+} to Fe^{2+}. Fenton reaction generates hydroxyl radicals and photo Fenton reactions reduce the Fe^{3+} to Fe^{2+} thus leading to the production of additional $OH^{\bullet}$ radicals and continuous regeneration of Fe^{2+} in a catalytic way.

$$H_2O_2 + h\nu \rightarrow OH^{\bullet} + OH^{\bullet} \quad\quad\quad (7)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow OH^{\bullet} + Fe^{2+} + H^+ \quad\quad\quad (8)$$
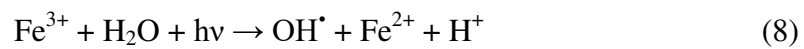
UV light has a dual advantage of generating additional hydroxyl radicals and also recycling of ferrous ions by reduction of ferric ions. This leads to an increase in the Fe2+ concentration, thus accelerating the overall reaction. The high efficiency of the photo-Fenton process to oxidize a variety of organic compounds, the simplicity of operation and the possibility of using solar light are advantages which can make the implementation easier of in situ and small scale treatment processes (Fonseca et al., 2010).

The photo-Fenton oxidation has many advantages compared to the classic Fenton reaction

- Higher rate of degradation

- Lower operational costs due to lower consumption of chemicals

- Minimal quantity of sludge formation, hence further reducing the operational cost which would occur during sludge removal and treatment.

The use of iron extracted from laterite soil, as a catalyst in Fenton reagent, has been reported by Mahmood (2013). The iron extracted from laterite soil is eco-friendly when compared to Fe^{2+} and is naturally available in most of the land area between the Tropic of Cancer and Tropic of Capricorn. In India, laterite soil is present in the eastern coastal region, covering the parts of Karnataka, Tamil Nadu and Orissa and small parts of Chota Nagpur Plateau in the North and Meghalaya in the North-East. The laterite soil contains 16 % to 67 % of the ferric oxide and is easily available.

2.2.2.3 Factors affecting Fenton and photo Fenton processes

There are several parameters and operational conditions which can substantially affect reaction rates and stoichiometry. These parameters have to be duly considered during the conduction of experiments, so as to achieve optimum conditions to ensure highest degradation rate.

Effect of pH

Fenton's oxidation process has been reported to have high efficiency in acidic medium. At pH 3, the observed removal is maximum, which may be due to the formation of $Fe(OH)^+$ which has higher activity than Fe^{2+} in Fenton oxidation (Mahamood 2013). When the pH is greater than 3, oxidation efficiency rapidly decreases due to auto-decomposition of H_2O_2 affecting the production of OH radical (Badway and Ali 2006) and deactivation of the ferrous catalyst with the formation of ferric hydroxide precipitates (Sun et al., 2007). Also, there is a decrease in the oxidation potential hydroxyl radical with an increase in pH value (Lucas and Peres 2006). When the pH is less than 3, the reaction of H_2O_2 with Fe^{2+} is affected that leads to a reduction in the hydroxyl radical generation and water is formed by the reaction of hydroxyl radical with H^+ ion (Muruganandham et al., 2004).

Effect of H₂O₂

The concentration of hydrogen peroxide plays an important role in the Fenton's oxidation reactions since it is the source of OH radicals that cause the degradation of organic compounds. The hydroxyl radicals either oxidize the pollutant and other intermediates or react with the oxidant itself to cause a reduction in the pollutant efficiency. The reaction rate increases with increase in the hydrogen peroxide concentration (Sun et al., 2007). The addition of H_2O_2 exceeding the optimum limit decreases the degradation efficiency. This may be attributed to the auto decomposition of H_2O_2 to oxygen and water, and the recombination of OH radicals. In addition, higher concentrations of hydrogen peroxide act as free-radical scavenger itself, which decreases the concentration of hydroxyl radicals and thereby reduces compound degradation efficiency (Mahamood 2013).

Effect of catalyst concentration (Fe²⁺)

Catalyst plays an important role in a reaction by providing a route that requires low activation energy, thereby increasing the rate of reaction. In Fenton's oxidation process, the degradation rate tends to increase with increasing Fe (II) concentration, up to the optimal dosage (Sun et al., 2007). The addition of iron salt above the optimal dosage does not affect the rate of degradation. When the Fe (II) concentration is higher than the optimum, the rate of hydroxyl radicals originated from the decomposition of H_2O_2 is so high that much of hydroxyl radicals are consumed by the side reactions before they are utilized for the removal of the pollutant. Moreover, it would result in the formation of a large compound sludge resulting in brown turbidity that hinders the absorption of the UV light required for photolysis and also would cause the recombination of OH radicals (Masomboon et al., 2011).

Effect of initial concentration of contaminant

The initial concentration of contaminant on the degradation is also an important parameter in Fenton's reaction. When the initial concentration of contaminant increases, the generation of $OH^•$ is not increased correspondingly, so a

relative lower OH$^•$ concentration resulted in a decrease in the degradation efficiency (Mahamood 2013).

2.2.3 Application of treatment processes for the removal of aniline derivatives

Brillas et al. (1997) studied the degradation of aniline in an acidic medium of pH 3 under photocatalytic and electrochemical conditions. Reduction in TOC was used to compare the efficiency of mineralization for each process. Special consideration was given to study the effect of Fe^{2+} ions and H_2O_2 on the process. Photoelectro-Fenton process was observed to have a higher aniline mineralization compared to Electro-Fenton process. The Fe^{2+} ions and H_2O_2 promoted faster mineralization during photocatalysis with TiO_2 at the initial stages. However, with longer irradiation time, they were found to hinder the mineralization process. A general reaction pathway that accounts for aniline mineralization to CO_2 involving those products was proposed.

Masomboon et al. (2010) investigated the oxidation of 2, 6-dimethylaniline by the electro-Fenton process in acidic solution at pH 2. The effect of pH, H_2O_2, Fe^{2+} and current density were determined to assess the optimum operating parameters. Reduction in the amount of 2, 6-dimethylaniline, COD and TOC was used to determine the oxidation efficiency. It was observed that 1mM of the compound required 1mM of Fe^{2+} and 20mM of H_2O_2 and a current density of 15.89Am^{-2} at pH 2 to achieve complete degradation in 4 hours. The highest COD and TOC removal were observed when 120 mM of hydrogen peroxide was used. Electro-Fenton process was found to be a reliable alternative for the degradation of 2, 6-dimethylaniline.

Kinetics of the 2, 6-dimethylaniline degradation was studied by Masomboom et al. (2011). In this study, the reaction kinetics of degradation of the compound by Fenton process, electro Fenton and photo electric Fenton process was investigated. Parameters like the initial concentration of the compound, ferrous ions and hydrogen peroxide were examined for their effect on the degradation. The results indicated that degradation of 2,6-dimethylaniline by electro Fenton process was higher than the ordinary Fenton and photo Fenton processes. Complete removal of 1mM 2,6-

dimethyaniline was obtained at 1 mM of ferrous ion, 20 mM of hydrogen peroxide, the current density of 15.89 Am^{-2} and 12 UVA lamps at pH 2.

Sun et al (2007) studied the degradation study of p-nitroaniline (PNA) in water by solar photo Fenton advanced oxidation process. The effect of different reaction parameters, such as pH, the dosage of hydrogen peroxide and ferrous ion, initial p-nitroaniline concentration were studied. The optimum conditions for the degradation of the PNA in water were found to be: pH value of 3, 10 $mmolL^{-1}$ H_2O_2, 0.05 $mmolL^{-1}$ Fe^{2+}, 0.072-0.217 $mmolL^{-1}$ PNA and temperature at 20^0C.it was found that the degradation efficiencies of PNA were more than 98% within 30 minutes at the optimum conditions. Solar photo Fenton process was found to have more advantages such as higher oxidation power, wide working pH range, lower ferrous ion dosage, etc compared to classical Fenton process.

The role of ferrous ion in Fenton and photo Fenton process for the degradation of phenol was studied by Kavitha et al. (2004). The efficiency of different Fenton-related oxidative processes such as Fenton, solar-Fenton and UV-Fenton was examined. Parameters that govern the Fenton's oxidation process were optimized and the different processes were compared for the degradation of phenol under there optimum conditions. The maximum mineralizing efficiency for phenol with Fenton, solar and UV-Fenton processes were 41%, 96% and 97% respectively. The end products like acetic acid and oxalic acid obtained in Fenton's oxidation process were almost completely oxidized after 120 minutes of photo-Fenton reaction. It was observed that photo-Fenton oxidation process had a higher degradation and mineralization efficiency as compared to conventional Fenton's oxidation process. Photo-Fenton process required half the amount of ferrous iron catalyst compared to the Fenton's oxidation process. To reduce the consumption of iron used in the Fenton's oxidation process, an iron reusability study was also performed.

Lu et al (2005) studied the effect of chloride ions on the degradation of aniline by Fenton reagent. Effect of pH, H_2O_2, Fe^{2+} and chloride concentration on oxidation reaction was investigated by conducting batch experiments. It was found that extending the reaction time could overcome the inhibition caused by chloride ions at low concentrations. At higher concentration of chloride ion, the oxidation of aniline is

inhibited. The inhibition was significant at the ratio of $[Cal^-]/[Fe^{2+}] \leq 200$. Also, the inhibition originating from chloride ion at an initial pH 3 could be overcome by addition of more amount of ferrous iron.

Liu et al (2011) investigated the treatment efficiency of aniline wastewater by comparing single photo-Fenton, single biological oxidation and combined photo-Fenton and biological oxidation. The effect of different factors, such as pH, Fe^{2+} and H_2O_2 concentrations on degradation efficiency were investigated. It was found that aniline wastewater was effectively degraded by the photo-Fenton process, but a large quantity of H_2O_2 was required to ensure complete mineralization. Hence, single photo-Fenton oxidation was deemed uneconomical. The aniline removal efficiency of is very low in direct biological oxidation due to its low biodegradability and toxicity to the microorganisms. Pretreatment of aniline wastewater by photo-Fenton oxidation considerably reduced its toxicity. Hence, combined photo-Fenton and biological oxidation was found to be effective treatment option for aniline wastewater. It was also found that, by combining these two processes, 62.5% of H_2O_2 was saved, compared to single photo-Fenton oxidation.

Table 2.3 Overview of Treatment Technologies Adopted for Removal of Aniline Derivatives from Wastewater (Mahamood, 2013)

	Physico-chemical processes	**Biological processes**	**Combined processes**
Processes	Coagulation, Adsorption, Chemical reduction processes, Reverse osmosis, Ion- exchange, Micro filtration, Electrochemical oxidation Fenton's reagent, ozone, Photo catalysis.	Pure cultures (fungal, bacterial and algal) mixed cultures, Aerobic & anaerobic	Physico-chemical/ AOP followed by biological, biological followed by physico-chemical/AOP. Sequential anaerobic-aerobic, integrated anaerobic - aerobic, a combination of physicochemical or biological processes.

2.3 SUMMARY OF THE LITERATURE

- Biological processes are reported to be cost effective and have many advantages over physical and chemical processes but are inefficient in complete removal and are time consuming. This is because aniline wastewater has low biodegradability and is toxic to microorganisms.

- Advanced oxidation processes (AOPs) are reported to be most effective in the removal of substances with low biodegradability like aniline derivatives.

- Removal of aniline has been reported using AOPs like Fenton, photo-Fenton, electro-Fenton, photoelectron-Fenton, anodic oxidation, ozonation and photocatalysis. The AOPs employed for removal of p-nitroaniline were found to be Fenton, Solar photo-Fenton and photocatalysis (TiO_2/UV and TiO_2/solar).

- Full-scale application of photocatalysis (TiO_2/UV) is still not spread due to both technical and economic reasons, mainly related to the proper handling of the catalyst.

- The Fenton and photo Fenton processes are easy to operate and can degrade most of the organic compounds. They appear to be more effective treatment methods for the removal of aniline derivatives.

- The release of reactive hydroxyl radical is a challenge for effective removal.

- Photo-Fenton (Fe^{2+}/H_2O_2/UV) oxidation studies have not been employed so far, for the removal of aniline derivatives. Also, comparative studies between Fenton and photo-Fenton oxidation processes have not been conducted till date.

- The maximum concentrations of PNA employed for degradation are found to be 0.217mM for Fenton and 1.16mM for solar photo Fenton respectively.

- Iron, Aluminium, cobalt and other metallic elements released from naturally available laterite/clay/Quartz enhance the oxidative potential.

- Iron extracted from laterite soil has been reported to be used as a catalyst instead of FeSO$_4$ in Fenton processes, without much change in treatment efficiency. Hence, it can be used as an alternative source of catalyst in this study, thereby reducing the cost of chemicals used.

2.4 LITERATURE GAP

- Fenton and Photo Fenton studies for 2 and 3-nitroanilines have not been reported in the literature so far.

- Photo-Fenton (Fe^{2+}/H$_2$O$_2$/UV) oxidation studies have not been reported from literature for PNA. Comparative studies between Fenton and photo-Fenton oxidation processes for PNA can be conducted.

- The maximum concentrations of PNA employed for degradation are found to be 0.217mM for Fenton and 1.16mM for solar photo Fenton respectively. So far, degradation studies have not been reported for a higher concentration of PNA. But in the textile industry effluent, PNA concentration is about 300mg/L. Hence degradation studies have to be conducted for higher concentrations.

- Iron extracted from laterite soil has been reported as an alternate catalyst instead of FeSO$_4$ in Fenton processes; hence, studies can be carried out using iron from laterite, for selected aniline derivatives which seem to be efficient and economical.

- Biological processes are slow and not effective enough to treat wastewater containing aniline derivatives. Hence Fenton and Photo Fenton oxidation can be used as an efficient alternative.

- Optimization of parameters is required to understand the mechanism of degradation of individual compounds which will help in further understanding the degradation pattern in the mixture.

- Degradation studies for a mixture of aniline derivatives have not been reported so far.

- Hence the degradation of aniline derivatives from wastewater is a great challenge to environmental scientists and engineers. Therefore novel and cost effective removal technologies have to be developed.

CHAPTER 3
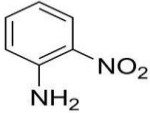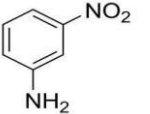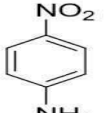
MATERIALS AND METHODS

This chapter presents the materials used and the detailed experimental methodology adopted in the study.

3.1 MATERIALS

The aniline derivatives used in this study are 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 2-Methoxyaniline and 4-Methoxyaniline. The physicochemical properties of the abovementioned aniline derivatives are presented in Table 3.1. Table 3.2 presents the instrument and the chemicals used in the study.

Table 3.1: Physicochemical characteristics of the selected aniline derivatives (http://www.inchem.org/documents/sids/sids/nitroaniline.pdf)

Aniline derivatives	Structure	Appearance	Molecular formula	Molecular weight (g/mole)	Solubility at 20^0C (g/L)	MP / BP (°C)
2-NA		Orange red solid	$C_6H_6N_2O_2$	138.12	1.1	70-73/ 284
3-NA		Yellow powder	$C_6H_6N_2O_2$	138.12	1.25	111-114/ 306
4-NA		Yellow fine crystal	$C_6H_6N_2O_2$	138.12	0.8	147/ 332
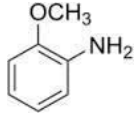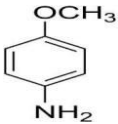
2-MA	OCH₃ NH₂	Reddish or brown liquid	C_7H_9NO	123.16	13	3-6/ 225
4-MA	OCH₃ NH₂	Dark grey crystal	C_7H_9NO	123.16	21	56-59/ 240- 243

Table 3.2: Instruments and chemicals used in the study

	Name	Details of Manufacturer
Instruments	High Performance Liquid Chromatograph	Agilent
	UV-VIS double beam spectrophotometer	Systronics
	pH meter	Lovibond
	Spectrophotometer visible range	Lovibond
Chemicals	2-Nitroaniline	Himedia
	3-Nitroaniline	Himedia
	4-Nitroaniline	Himedia
	2-Methoxyaniline	Himedia
	4-Methoxyaniline	Himedia
	Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$)	Himedia
	Hydrogen peroxide (H_2O_2) 50% w/w	Merck (India)
	Sulphuric acid (H_2SO_4)	Merck (India)
	Sodium Hydroxide (NaOH) 98% purity	Merck (India)
	Hydrochloric acid (HCl), 35% purity	Merck (India)
	Potassium thiocyante (KSCN)	Merck (India)

Ammonium nitrate	Merck (India)	
Ammonium molybdate	Merck (India)	
Potassium dichromate ($K_2Cr_2O_7$)	Merck (India)	
Silver Sulphate ($AgSO_4$)	Merck (India)	
Mercuric Sulphate	Merck (India)	
1,10 phenanthroline monohydrate	Merck (India)	
Potassium iodide (KI)	Merck (India)	
Sodium thiosulphate ($Na_2S_2O_3$)	Merck (India)	
Ferrous ammonium sulphate	Himedia	

3.2 EXPERIMENTAL METHODOLOGY

3.2.1 Spectral and chemical characterization of the model parameters

UV-VIS spectrum is recorded using UV-VIS double beam spectrophotometer. The absorbance peaks are observed to be at wavelengths 282nm, 227nm, 380nm, 282.5 and 296nm for 2-NA, 3-NA, 4-NA, 2-MA and 4-MA respectively. For the range of concentrations considered for each drug, a linear relationship (calibration curve) between absorbance and concentration are established. These calibration curves are used to measure the pollutant concentration before and after treatment.

3.2.2 Fenton Oxidation

The experiments are conducted at ambient temperature ($27\pm3^{o}C$) in batch rectors. A 1000 mL solution of required concentration is prepared from the stock solution and taken in a 2L long beaker (reactor). An appropriate amount of Fe^{2+} concentration from the 1000 mg/L stock solution, freshly prepared from $FeSO_4.7H_2O_2$ is added to the reactor and stirred in magnetic stirrer. The required amount of hydrogen peroxide is added to the reactor bath to initiate the reaction. Initial pH of the solution is maintained using 0.1N H_2SO_4 and 6N NaOH. Fenton's treatment of a

simulated aqueous solution containing the selected pollutant is conducted for a period of 2hrs. After 24 hrs of reaction period the treated samples are taken for various analyses. The optimum Fenton's dosage for maximum degradation is found out by varying concentration of iron and hydrogen peroxide. Continuous mixing is done with a magnetic stirrer for 2 hrs. After the reaction period, some quantity of the treated solution is taken for analysis. Further above steps are repeated for iron extracted from laterite soil in place of ferrous sulphate as an iron source.

3.2.3 Optimization of pH

The pH of the solution is an important parameter for Fenton's oxidation process, which controls the production rate of hydroxyl radical and the concentration of Fe^{2+}. It is also an important operational variable in actual wastewater treatment. In order to find the optimal pH of the effective degradation of Nitroaniline & Methoxyaniline in Fenton's oxidation, a set of experiments is conducted. At the beginning of the experiment, pH is adjusted to 2-4 with an interval of 0.5 pH unit by using 6N NaOH and 0.1N H_2SO_4, which is followed by the addition of Fenton reagent. Nitroaniline and Methoxyaniline concentrations of 0.5mM, ferrous sulphate of 0.05mM and H_2O_2 of 3.5mM are taken for this experiment. Reaction volume is 1000 ml. It is continuously stirred at room temperature in an open batch system with a magnetic stirrer for 2 hr. The pollutant concentration and COD values are measured after 24hrs of reaction time. The pH at which pollutant removal, as well as mineralization, is maximum is chosen at optimum pH and all other sets of experiments are conducted at this optimized pH.

3.2.4 Optimization of hydrogen peroxide and iron concentration

Hydrogen peroxide is the basis for the radical generation in Fenton's oxidation. The ratios of H_2O_2 & Fe^{2+} are important for the degradation of pollutant in Fenton & photo Fenton process. Hence an investigation of H_2O_2 consumption and optimization in Fenton's oxidation is vital for using H_2O_2 efficiently and also for the other best possible conditions that were to be found in the process. So after optimizing

the pH set of experiments were conducted for 4-NA, 2-MA to optimize the Fenton's dosage.

3.2.5 Photo Fenton oxidation

Photo Fenton oxidation experiments were carried out using photo reactor consists of 8W UV-C Philip lamp covered with quartz jacket which is connected to AC power and stirred using magnetic stirrer. All the experiments were carried out at ambient temperature in batch mode. The experiments were carried out for the previously optimized dosages of the Fenton's oxidation experiments. A 1000 ml solution of the required pollutant concentration is prepared using stock solution and taken in a 1L long beaker and pH was adjusted to required level. The previously optimized dosages of iron and hydrogen peroxide are added and UV-C lamp and the magnetic stirrer is switched on. After the reaction period, the supernatant of the solution is taken out for analysis and filtered through 0.45 μm filter paper. The concentration of the pollutant, residual hydrogen peroxide and COD was measured and removal efficiencies were calculated

3.2.6 Kinetics studies on the aniline derivatives

The kinetic studies were carried out for 0.5mM pollutant concentration at the optimized dosages for 120 mins at an interval of 10 mins. The kinetic studies of the 0.5mM concentration are carried out for both Fenton and Photo-Fenton oxidation using $FeSO_4$ and iron extracted from laterite soil

3.2.7 Mixture of aniline derivatives compound

In actual field conditions, the wastewater contains the mixture of nitro aromatic compounds hence in order to simulate the wastewater into the real effluent, studies on the mixture of aniline derivatives are carried out. The mixture of the solution is prepared for the 0.5mM initial concentrations of each compound and mixed together. Further, the pH of the mixture is optimized by varying the pH in the range of 2-4.

After optimization of the pH, the hydrogen peroxide dosage was optimized by varying the concentration between 5mM-18mM. After optimizing the hydrogen peroxide iron concentration was varied from 0.025-0.1mM. The studies were continued for the iron extracted from laterite. The photo Fenton oxidation studies were carried out at optimized dosages obtained during Fenton's oxidation and also using the iron extracted from laterite.

3.2.8 Analytical Methods

Standard solutions of aniline derivatives are prepared and UV-VIS spectra are recorded from 200-500nM using UV-VIS double beam spectrophotometer (Systronics - 2201). The pH is measured with a digital pH meter (Lovibond - pH meter). The COD of the samples is determined by closed reflux titrimetric method as per the procedure outlined in Standard Methods (APHA, 2005). The iron concentration is measured using spectrophotometer (Lovibond) by thiocyante–colorimetric method. The H_2O_2 concentration is determined by iodometric titration method.

3.2.8.1 pH

The pH value is defined as the negative common logarithm of the activity of the positively charged hydrogen ion in aqueous solution. Whenever the pH value of a solution is reported this data should be accompanied by the temperature at which it was measured. For the measurement of pH, a Sensodirect pH 100meter (Lovibond Germany) is used. The measurement of pH is carried out by submersing the electrode and waiting until the instrument reached equilibrium.

3.2.8.2 Chemical Oxygen Demand (COD)

The COD is determined to evaluate the degree of mineralization of the selected pollutant concentration during AOP process. For the digestion of COD sample in COD determination, COD digester –ET 125 (Lovibond, Germany) is used. The FAS titrant is prepared with a molarity of 0.025. The COD of the sample is

determined by closed reflux titrimetric method (5220 C) as per the procedure outlined in the Standard Methods (APHA 2005)

$$COD \text{ as mg } O_2/L = [(A-B) \times M \times 8000]/ [ml \text{ of sample}]$$

$$\text{where } A = ml \text{ of FAS used for blank}$$

$$B = ml \text{ of FAS used for the sample}$$

$$M = \text{Molarity of FAS}$$

$$8000 = \text{milliequivalent weight of oxygen} \times 1000mL/L$$

Initial and Final COD was measured and % COD removal was calculated by (Initial COD- Final COD) /Initial COD

3.2.8.3 Hydrogen Peroxide (H_2O_2)

H_2O_2 concentration in the sample is determined by Iodometric titration method. Iodometry can be applied to measure many oxidizing agents. The principle is that an excess of iodine is added to the sample in acidic condition. Then the oxidizing agent reacts quantitatively with the iodine in the form of the stoichiometric equivalent amount of triiodine anions. By titration, the amount of triiodine anion formed is determined by addition of thiosulphate, which reacts quantitatively to tetrathionate. Starch forms a blue-grey complex with the triiodine ion. Consequently, in the presence of starch as an indicator, the complete disappearance of the triiodine ion can be visually observed since assay colour changes from dark blue-grey to transparent. The method is less accurate than the permanganate titration, but is less susceptible to interference by organics and is more suitable for measuring of H_2O_2. The other oxidizing agent will also produce iodine but the reducing agents will react with the liberated iodine. The contribution from these oxidizing agents can be omitted by acid and molybdate catalyst.

Typically 25ml of the sample is taken in conical flak. 10ml of H_2SO_4 (20%) and 10-15ml KI solution and then 2 drops of ammonium molybdate are added to the sample. Upon addition of iodine solution in the presence of the oxidant, the solution becomes dark yellow. The solution is kept for 20-30 minutes at room temperature in a

closed bottle protected from light. The sample mixture is titrated with 0.1N sodium thiosulphate till colour changes to straw yellow colour. Then the 2-5 drops of starch solution were added as an indicator. The solution becomes dark blue upon the addition of starch solution. Subsequently, titration is continued with 0.1N $Na_2S_2O_3$. The hydrogen peroxide concentration can be calculated assuming that all oxidation of iodine to triiodine ion is due to its presence.

$$C_{H2O2} = [V_{Na2S2O3}/ V_{sample}] \times 1700 \text{ mg/L}$$

3.2.8.4 Iron concentration

The iron may exist in both ferrous and ferric forms. The form of iron may be altered as a result of oxidation or reduction. Normally ferrous iron is dissolved in water and ferric iron readily settles. Oxidizing agents (such as hydrogen peroxide) interfere with the test because they oxidize ferrous iron to ferric iron, which does not form complexes with the reagent. The ferric iron combines with thiocyante ion to form a red coloured ferric Thiocyante that can be measured colorimetrically at 510nm.

Series of standard iron solutions ranging from 0.5-2.5mg/L are prepared using ferrous ammonium sulphate. Each iron standard is mixed with 4ml 4N HCl. 5ml 5% KSCN and made to 100ml with distilled water in Nessler's tube. The spectrophotometer is calibrated using these standards by setting the wavelength at 510 nm and the method is stored in it. AOP treated solution is thoroughly mixed and about 10-20ml of sample is taken in the Nessler's tube, to this 4ml 4N HCl, 5ml 5% KSCN and the solution is made up to 100ml with the sample. The mixture is thoroughly mixed and kept for 15minutes to develop a stable orange colour. Then the sample is measured in a spectrophotometer.

3.2.8.5 Extraction of Iron from Laterite Soil by Leaching with HCl

Iron is extracted from laterite soil as per the procedure explained by Olannipekun (2000). Laterite soil for the extraction of iron is taken from NITK,

Surathkal campus. The dried laterite soil is crushed to powder and is passed through 150 micron sieve. 0.5g of the sieved soil sample is taken in a glass beaker and 20ml of 1:1 HCl is added. This solution is mixed and grinded till the entire sample is dissolved completely. The sample is kept on a hot plate for maximum evaporation till the residue is formed. The residue left is baked in an oven for 1 hour and 20ml of 1:1 HCl is added and it is heated for 1 minute, following which, 20ml of hot distilled water is added. The solution is filtered through a Whatman 42 filter paper and the filtrate obtained is transferred to Nessler's cylinder and diluted up to 100ml, the solution obtained is the iron extracted from the laterite soil.

3.2.8.6 HPLC Analysis

Samples are analysed using High Performance Liquid Chromatography (HPLC) at $22 \pm 0.5°C$. The Agilent Binary LC is used in this study which is fitted with a reversed phase ZORBAX C18 silica (100mm 4.6 mm, 3.5 micron pore size) column. The diode array detector (DAD) is to be set to the required adsorption wavelength. The representative HPLC chromatogram is obtained from the analysed solution. The samples are filtered through a 0.2μm filter before HPLC analysis to prevent small particles from blocking the capillary and valves. The operational conditions adopted to carry out the analysis are given in Table 3.3.

Table 3.3 Operational conditions for HPLC analysis of aniline derivatives

Selected pollutant	Wavelength	Injection volume (μL)	Column Temperature (^{0}C)	Methanol: DW ratio	Flow rate (ml/min)	Retention Time obtained (mins)
2-NA	282	20	30	50:50	0.5	6.2
3-NA	227	20	25	70:30	1	6.1
4-NA	380	20	30	55:45	1	1.6
2-MA	282	20	25	70:30	1	1.4
4-MA	296	20	25	65:35	1	1.3

CHAPTER 4

RESULTS AND DISCUSSION

As stated in chapter 1, the primary objective of the present study is to develop a cost effective process for the removal of selected aniline compounds normally found in wastewater generated from textile industries. This chapter presents the details of studies carried out using details of the studies carried out using conventional Fenton's and Photo-Fenton oxidation process and optimised parameters which influence the efficiency of the process. The major highlight of the present study is to reduce the cost and hence iron extracted from locally available laterite replaced iron salts. This chapter presents the experimental results to understand the efficiency of such replacement. Further the results pertaining to kinetics and degradation of a mixture of aniline compounds are also reported in this chapter. Further, the results presented are the average of duplicate observations. The results are presented in the form of tables and figures.

4.1 FENTON'S OXIDATION

4.1.1 Fenton oxidation of 2-Nitroaniline

4.1.1.1 Effect of pH

The pH of the solution is an important parameter for Fenton's oxidation process, which controls the production rate of hydroxyl radical and concentration of Fe^{2+}. It is also an important operational variable in actual wastewater treatment. In order to find the optimal pH of the reaction mixture for the degradation of 2-Nitroaniline on Fenton's oxidation experiments were conducted at different pH values ranging from 2 to 4 with an initial concentration of 0.5 mM which is illustrated in Figure 4.1.
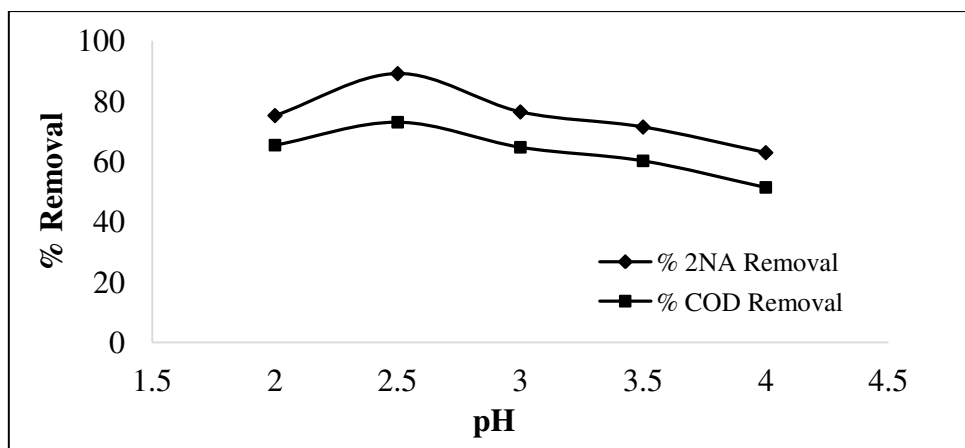
Figure 4.1: Effect of pH on removal of 2-Nitroaniline (2-NA concentration: 0.5mM, H_2O_2 dosage: 3.5mM, Fe^{2+}dosage: 0.05mM, Reaction Time =5hrs)

Figure 4.1 shows the % 2-NA and % COD removal of initial concentration 0.5mM at different pH keeping the ratio H_2O_2: Fe^{2+}::3.5:0.05. The removal of 2-NA was maximum at pH 2.5 compared to all other pH values between 2.0 to 4.0. The maximum 2-NA removal of 89.1% and COD removal of 73% was obtained at pH 2.5. At pH 3, 3.5 and 4 removal efficiency was reduced indicating the optimum pH of 2.5. It can be observed that removal efficiency increases initially with an increase in the pH and till it reaches the optimum pH and removal efficiency decreases with further increase the pH.

When pH is more than the optimum value, oxidation efficiency rapidly decreased, not only by decomposition of hydrogen peroxide but also by deactivation of a ferrous catalyst with the formation of ferric hydroxide complexes leading to a reduction of OH radical.

Another reason for the inefficient degradation at pH greater than optimum value is due to the dissociation and auto-decomposition of H_2O_2 (Badawy and Ali, 2006). For pH values below 2.5, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected causing the reduction in hydroxyl radical production. The low degradation at pH 1 and 2 is due to the hydroxyl radical scavenging of H^+ ions (Lucas and Peres, 2006).

Another possible explanation for the oxidation inhibition at pH lower than optimum is based on the main Fe^{3+} soluble species in equilibrium which shown in the equation below.

$$Fe^{2+} \rightarrow Fe^{3+} \Leftrightarrow Fe(OH)^{2+} \Leftrightarrow Fe(OH)^{+}_{2}$$
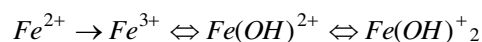
At optimized pH more $Fe(OH)^{+}$ is formed, which has much higher activity as compared to Fe^{2+} in Fenton's oxidation. Also at the higher pH, H_2O_2 loses its oxidizing potential (Malik and Saha, 2003).

In addition, during optimum pH, the hydrogen peroxide gets solvated in the presence of high concentration of hydrogen ion (low pH) to form stable oxinium ion (Elmolla and Chaudhari, 2009).

4.1.1.2 Effect of H_2O_2

The amount of hydrogen peroxide and ferrous ion are important parameters to influence the Fenton's oxidation process. Figure 4.2 shows the 2-NA removal and COD removal by varying the hydrogen peroxide dosage for 0.5mM of 2-NA concentration. The hydrogen peroxide dosage was varied from 2.0mM to 4.0mM keeping the iron concentration constant. In this study to obtain the optimal concentration, the investigation was carried by varying the iron concentration from 0.025 mM to 0.275 mM at pH 2.5 with keeping hydrogen peroxide concentration constant for the initial concentration of 0.5mM.
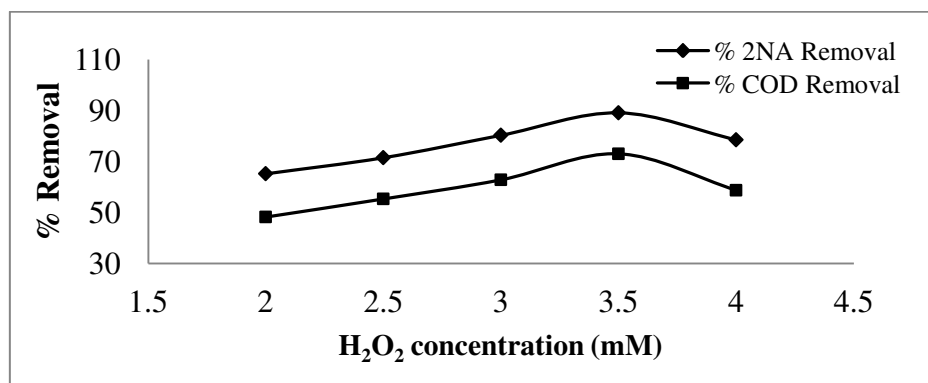
Figure 4.2: Effect of H_2O_2 concentration on removal of 2-Nitroaniline (2-NA dosage: 0.5mM, Fe dosage: 0.05mM, pH = 2.5, Reaction Time = 5hrs)

Figure 4.2 shows the 2-NA and COD removal efficiencies for 0.5 mM of 2-NA concentration. For 0.5 mM 2-NA concentration, the H_2O_2 concentration was varied from 2.0 - 4.0 mM keeping Fe concentration constant as 0.05mM, maximum removal of 89.1% and COD removal of 73% was obtained at 3.5 mM H_2O_2. When the H_2O_2 concentration was 2.0mM, the removal was found to be 65.2% and 48.2% for 2-NA and COD respectively. Then the H_2O_2 concentration is increased to 2.5mM and removal efficiencies obtained was 71.5 % and 55.3% respectively for 2-NA and COD removal. Further studies were carried out for 3.0mM, 3.5mM and 4.0mM of H_2O_2 concentration. The removal efficiencies obtained for 3mM of H_2O_2 concentration are 80.3% and 62.8% respectively for % 2-NA and COD removal. The maximum removal of 89.1% and COD removal of 73% was obtained at 3.5mM H_2O_2. Then for 4.0mM of H_2O_2 concentration the % 2-NA and COD removal obtained was 81.9% and 58.7% respectively. As the H_2O_2 concentration increased to 4.0mM, the 2-NA and COD removal was reduced as shown in Figure 4.2. Similarly, for 1.0mM of 2NA, H_2O_2 concentration was varied from 4.0-8mM and maximum removal of 88.3 % and COD removal of 69.1 % was observed at 7.5mM and Fe concentration of 0.1mM. Then for 1.5mM concentration, the H_2O_2 concentration was varied from 8.0mM to 12.5mM, Fe concentration was kept constant as 0.15mM. The maximum removal of 86.4 % and COD removal of 65.4% was obtained at H_2O_2 concentration of 12.0mM. For the 2.0mM 2-NA concentration, the hydrogen peroxide dosage was varied from 12.5mM-17.0mM keeping Fe as 0.2mM. The maximum 2-NA removal of 81.4 % and COD removal of 61.6 % was obtained at 16.5mM of H_2O_2. Further for 2.5mM of 2-NA concentration H_2O_2 concentration was varied from 17.0 to 21.5mM, Fe concentration was kept constant as 0.25mM. The maximum 2-NA and COD removal obtained were 78% and 58.2% respectively. All the experiments were carried out for a reaction period of 5hrs. Residual H_2O_2 was negligible after the reaction period. Table 4.1 provides the maximum 2-NA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration. Hence the optimum H_2O_2 concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 2-NA concentration were 3.5mM, 7.5mM, 12mM, 16.5mM and 21mM respectively.

Table 4.1: Effect of H₂O₂ concentration on removal of 2-NA with different initial concentration at constant Fe²⁺ dosage

2-NA (mM)	Fe²⁺ (mM)	H₂O₂ (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	2	65.2	48.2	40
		2.5	71.5	55.3	50
		3.0	80.3	62.8	60
		3.5	**89.1**	**73.0**	**70**
		4.0	81.9	58.7	80
1.0	0.1	4	65.1	55.1	40
		4.5	70.1	58.1	45
		5.0	73.7	60.7	50
		5.5	75.6	63.3	55
		6	78.5	65.6	60
		6.5	81.6	66.7	65
		7	85.7	68.16	70
		7.5	**88.3**	**69.1**	**75**
		8	84.5	62.5	80
1.5	0.15	8	63.2	45.5	53.4
		8.5	65.5	48.9	56.6
		9	70.5	53.5	60
		9.5	73.1	54.3	63.3
		10	76.5	56.2	66.6
		10.5	78.1	57.2	70
		11	81.3	59.1	73.3
		11.5	83.5	60.1	76.6
		12	**86.4**	**65.4**	**80**
		12.5	84.5	61.8	83.3
2.0	0.2	12.5	61.5	43.2	62.5
		13	63.2	46.7	65
		13.5	65.7	48.8	67.5
		14	67.5	49.5	70

		14.5	70.5	50	72.5
		15	72.8	53.1	75
		15.5	74.3	55.3	77.5
		16	77.5	58.6	80
		16.5	**81.4**	**61.6**	**82.5**
		17	78.4	59.2	85
		17	60.5	42.5	68
		17.5	61.5	45.7	70
		18	61.1	46.9	72
		18.5	66.1	47.6	74
2.5	0.25	19	68.7	49.8	76
		19.5	71.6	51.5	78
		20	72.7	53.8	80
		20.5	76.5	56.3	82
		21	**78**	**58.2**	**84**
		21.5	75	56.5	86

However, with continuous increasing of the H_2O_2, the degradation rate of 2-NA reduced. This may be explained by the fact that the very reactive OH radical could be consumed by H_2O_2 and results in the generation of less reactive OOH radical (Chen and Pignatello, 1997; Kang et al., 2002; Walling and Kato, 1971; Muruganandham and Swaminathan, 2004). Hsueh et al. (2005) explained one more possible reason for the reduction in the 2-NA removal.

As H_2O_2 concentration increases, reduction in the removal was also observed, which may be due to the hydroxyl radical scavenging effect of H_2O_2 according to equations below.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2{}^{\bullet}$$

$$HO_2{}^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2$$

$$ {}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$$

According to Hsueh et al. (2005), the degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, when a concentration higher than the critical concentration is used, the degradation rate of organic compounds was decreased as a result of so-called scavenging effect.

4.1.1.3 Effect of Fe^{2+} Concentration

The iron concentration was optimized after optimization of H_2O_2 dosage by varying the iron dosage. The Fe concentration was varied from 0.025-0.125mM for the initial concentration of 0.5mM of 2-NA keeping H_2O_2 dosage constant as 3.5mM. The experiments were conducted at previously optimized hydrogen peroxide concentration. For the 0.5mM concentration of 2-NA, the Fe concentration was varied from 0.025mM -0.1mM at an interval of 0.025mM keeping H_2O_2 dosage as 3.5mM. The maximum 2-NA removal of 89.1 % and COD removal of 73% was obtained at 0.05mM Fe concentration. As iron concentration increased from 0.025 to 0.05mM, degradation was increased. For initial Fe concentration of 0.025mM, the 2-NA removal was 81.1% and COD removal was 56.4%. The maximum removal efficiencies were obtained at a concentration of 0.05mM. Then the 2-NA and COD removal were decreased at Fe concentration of 0.075mM, the removal efficiencies obtained for 0.075mM of Fe concentration was 78.3% of 2-NA removal and 63.4% of COD removal which is as shown in Figure 4.3. Table 4.2 presents the results of 2-NA and COD removal efficiencies as a function of Fe^{2+} concentration at different initial concentrations with constant H_2O_2 dose.

Figure 4.3: Effect of Fe concentration on removal of 2-Nitroaniline (2-NA dosage: 0.5mM, H₂O₂ dosage: 3.5mM, pH = 2.5, Reaction Time =5hrs)

Table 4.2: Effect of Fe $^{2+}$ concentration on different initial concentration of 2-NA at constant H₂O₂ dosage

2-NA (mM)	H₂O₂ (mM)	Fe^{2+} (mM)	% Removal	% COD removal	H/F ratio
0.5	3.5	0.025	81.1	56.4	140
		0.05	**89.1**	**73**	**70**
		0.075	79.8	62.2	46.6
		0.1	72.1	55.6	35
1	7.5	0.05	80.6	58.5	150
		0.075	82.1	61.3	100
		0.1	**88.3**	**69.1**	**75**
		0.125	82.3	60.1	60
1.5	12	0.1	71.5	50.5	120
		0.125	80.2	58.2	96
		0.15	**86.4**	**65.4**	**80**
		0.175	75.6	46.3	68.5
2.0	16.5	0.15	71.1	42.2	96.6
		0.175	78.1	50.6	82.8
		0.2	**81.4**	**61.6**	**82.5**

		0.225	76.5	52.1	64.4
2.5	21	0.2	70.8	43.5	105
		0.225	73.8	47.5	93.3
		0.25	**78.0**	**58.2**	**84**
		0.275	75.7	50.4	76.3

Similarly, studies were conducted for the different initial concentrations of 2-NA. For 1.0mM of 2-NA, Fe concentration varied from 0.05-0.125mM and maximum removal of 88.3% and COD removal of 69.1% was obtained at 0.1mM of Fe concentration. Then for 1.5mM of 2-NA concentration, Fe concentration varied from 0.1-0.175mM and optimized Fe concentration was 0.15mM. The maximum removal of 86.4% and COD removal of 65.4% were obtained. Then the initial concentration of 2-NA is increased to 2.0mM and Fe concentration varied from 0.15mM-0.225mM, the maximum 2-NA removal of 81.4% and 61.6% of COD removal is obtained at Fe concentration of 0.2mM. Then for 2.5mM initial concentration of 2-NA, Fe concentration was varied from 0.2-0.275mM. The maximum 2-NA removal and COD removal were 78% and 58.2% respectively for 0.25mM of Fe concentration at optimized hydrogen peroxide concentration of 21mM. When the concentration of Fe^{2+} was higher, a great amount of Fe^{3+} from the process of H_2O_2 decomposition by Fe^{2+} was easy to exit in the form of $Fe(OH)^{2+}$ in the acidic environment. As it can be seen, the effect of increasing H_2O_2 was first positive for the degradation of 2-NA. The optimum dosages of the iron concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 2-NA concentration were 0.05, 0.1, 0.15, 0.2, 0.25mM respectively. Optimum Fenton's dosage for each initial concentration of 2-NA and the respective % 2-NA removal and % COD removal are summarized in Table 4.3.

Table 4.3: Optimum dosages obtained during Fenton's oxidation of 2-Nitroaniline

Initial 2-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} concentration (mM)	2-NA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	89.1	73	70
1.0	7.5	0.1	88.3	69.1	75
1.5	12.0	0.15	86.4	65.4	80
2.0	16.5	0.2	81.4	61.6	82.5
2.5	21	0.25	78	58.2	84

The degradation of 2-Nitroaniline can be well supported by comparing the UV-VIS spectrum of the sample before and after treatment. The UV-VIS spectrum obtained before treatment has a peak at 282nm in UV region as seen in Figure. A2. But, in the UV-VIS spectrum of treated sample, a peak at 282nm disappeared, indicating the degradation of 2-Nitroaniline in Fenton's oxidation.

The HPLC analysis was carried out for the 2-NA for 0.5-2.5mM concentration at an optimum dosage. The chromatograph for 2-NA before and after treatment are shown in Figure A13 & A14. The retention time obtained for 4-NA was 6.2 minutes, whereas, after Fenton's treatment under optimum conditions, the chromatograph obtained is as shown in Figure A14 and it indicates that, no peak was observed at a retention time of 6.2 minutes i.e. the 2-NA is degraded completely. This confirms the experimental results reported earlier.

4.1.2. Fenton oxidation of 3-Nitroaniline

4.1.2.1 Effect of pH

Figure 4.4 shows the effect of pH on 3-NA and COD removal. The study was carried out for 0.5mM of initial 3-NA concentration keeping the ratio H_2O_2: Fe^{2+}:: 3.5:0.05. The maximum removal efficiencies of 78.5% and 62.7% for 3-NA and COD

were obtained at pH 2.5. The removal efficiencies decreased after the pH 2.5.Hence the optimized pH for the 3-NA was 2.5.

Figure 4.4: Effect of pH on removal of 3-Nitroaniline (3-NA concentration: 0.5mM, H$_2$O$_2$ dosage: 3.5mM, Fe dosage: 0.05mM, Reaction Time =5hrs)

4.1.2.2 Effect of H$_2$O$_2$ Concentration

The investigation for optimization of hydrogen peroxide concentration was carried out by varying H$_2$O$_2$ concentration, keeping iron concentration for initial 3-NA concentration at optimum pH of 2.5. Initially for 0.5 mM of 3-NA solution, the Fe concentration was kept constant as 0.05 mM and H$_2$O$_2$ concentration was varied from 2.5 mM to 5 mM. When the concentration was 2.5 mM the corresponding 3-NA removal and COD removal observed were 70.4% and 50.2% respectively. Then the H$_2$O$_2$ concentration increased to 3.0mM and the % 3-NA and % COD removal observed was 75.6% and 58.2% respectively. Next, the studies were carried by increasing the H$_2$O$_2$ concentration to 3.5 mm, 4.0 mM, 4.5 mM and 5 mM. The removal efficiencies obtained for 3.5mM and 4mM was 78.5%, 62.7% and 85.6%, 66.7% respectively for 3-NA and COD removal. Further for 4.5mM and 5.0mM concentration of hydrogen peroxide, the 3-NA and COD removal efficiencies obtained were 88.7%, 71.7% and 84.5% and 64.2% respectively. The maximum 3-NA removal is observed to be 88.7% and corresponding COD removal is 71.7% for

45

0.5mM initial 3-NA concentration at H_2O_2 concentration of 4.5mM after the reaction time is shown in Figure 4.5. Hence the optimum H_2O_2 concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 2-NA concentration were 3.5mM, 7.5mM, 12mM, 16.5mM and 21mM respectively.
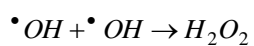

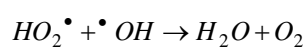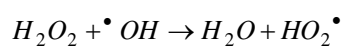**Figure 4.5: Effect of H_2O_2 concentration on removal of 3-Nitroaniline (3-NA dosage : 0.5 mM, Fe concentration: 0.05 mM, pH = 2.5, Reaction Time =5hrs)**

In the beginning, the 3-NA concentration and COD removal increased up to the maximum value with increase in H_2O_2 concentration and further increase in H_2O_2 concentration decreased the removal efficiencies. This may be due to the production of less number of OH radical when H_2O_2 is less than optimized concentration, on the other hand when H_2O_2 is greater than optimum value, the degradation and mineralization are less because of the scavenging effect of OH radicals with an increase in the H_2O_2 concentration. This can be explained by the fact that the very reactive OH radicals are scavenged by the increased H_2O_2 that results finally into water. Table 4.4 provides the maximum 3-NA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration.

Table 4.4: Effect of H$_2$O$_2$ concentration on different initial concentration of 3-NA at constant Fe^{2+} dosage

3-NA (mM)	Fe^{2+} (mM)	H$_2$O$_2$ (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	2.5	70.4	50.2	50
		3.0	75.6	58.2	60
		3.5	78.5	62.7	70
		4.0	85.6	66.7	80
		4.5	**88.7**	**71.7**	**90**
		5.0	84.5	64.2	100
1.0	0.1	5.0	65.9	50.1	50
		5.5	68.8	51.2	55
		6.0	69.6	52.3	60
		6.5	72.1	54.5	65
		7.0	75.2	57.4	70
		7.5	77.3	59.6	75
		8.0	79.4	61.7	80
		8.5	82.5	63.8	85
		9.0	84.6	64.9	90
		9.5	**86.9**	**66.4**	**95**
		10.0	83.5	63.5	100
1.5	0.15	10.0	61.1	43.2	66.6
		10.5	65.2	45.3	70
		11.0	67.3	47.4	73.3
		11.5	70.4	49.5	76.6
		12.0	73.5	51.7	80
		12.5	75.6	54.2	83.3
		13.0	77.8	57.5	86.6
		13.5	80.6	59.6	90
		14.0	82.8	61.7	93.3
		14.5	**84.7**	**63.4**	**96.6**
		15.0	81.5	60.5	100

		15.0	59.2	38.3	75
		15.5	61.3	40.8	77.5
		16.0	63.8	41.4	80
		16.5	65.4	45.5	82.5
		17.0	67.9	47.3	85
2.0	0.2	17.5	70.8	50.4	87.5
		18.0	73.5	51.3	90
		18.5	75.6	55.2	92.5
		19.0	77.3	58.1	95
		19.5	**79.3**	**60.1**	**96.6**
		20.0	76.9	58.9	100
		20.0	58.2	39.9	80
		20.5	60.3	41.8	82
		21	61.4	43.7	84
		21.5	63.5	45.6	86
		22.0	66.9	46.5	88
2.5	0.25	22.5	68.8	48.4	90
		23.0	70.7	50.5	92
		23.5	71.8	52.6	94
		24.0	73.9	54.8	96
		24.5	**76.5**	**56.3**	**98**
		25.0	74.5	53.5	100

4.1.3.2 Effect of Fe^{2+} Concentration

The H_2O_2 concentration is kept constant as 4.0mM for 0.5mM of 3-NA concentration and Fe dosage was varied from 0.025-0.1mM. For 0.025mM of Fe concentration the % 3-NA removal and % COD removal obtained was 80.2% and 64.2%. The maximum 3-NA removal is 88.7% and corresponding COD removal is 71.7% at 0.05mM of Fe^{2+} concentration and the same can be seen in Figure 4.6. Then the studies were further carried out for Fe concentration of 0.075mM, 0.1mM and corresponding removal efficiencies are 81.5%, 62.4% and 75.2%, 56.5% respectively for % 3-NA removal and % COD removal. Table 4.5 presents the results of 3-NA and

COD removal efficiencies as a function of Fe^{2+} concentration at a different initial concentration at constant H_2O_2.
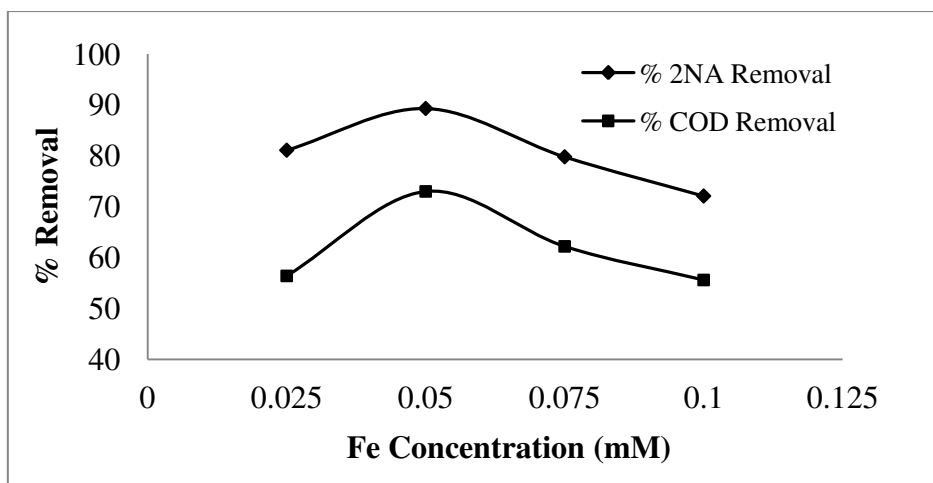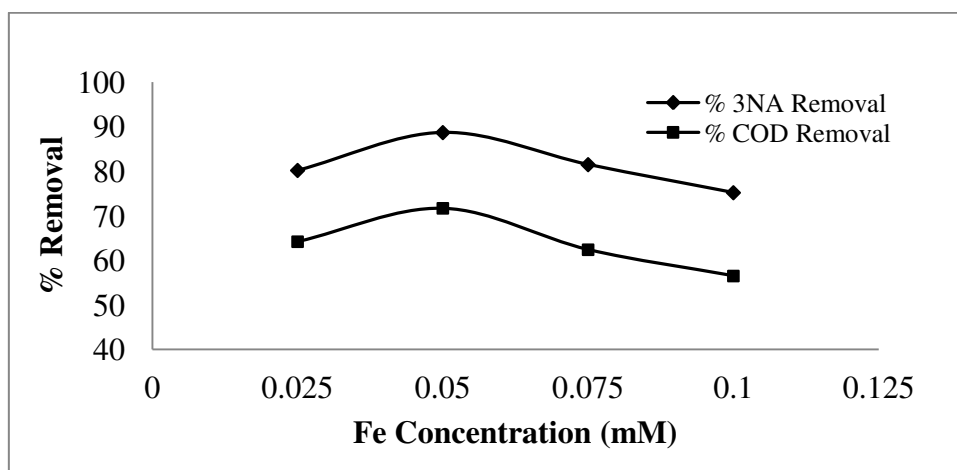

Figure 4.6: Effect of Fe concentration on removal of 3-Nitroaniline (3NA concentration: 0.5mM, H_2O_2 dosage: 4.5mM, pH = 2.5, Reaction Time =5hrs)

Table 4.5: Effect of Fe $^{2+}$ concentration on different initial concentration of 3-NA at constant H_2O_2 dosage

3-NA (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	% Removal	% COD removal	H/F ratio
0.5	4.5	0.025	80.2	64.2	180
		0.05	**88.7**	**71.7**	**90**
		0.075	81.5	62.4	20
		0.1	75.2	56.5	15
1	9.5	0.05	80.2	60.5	190
		0.075	83.3	63.7	126.6
		0.1	**86.9**	**66.4**	**95**
		0.125	82.5	61.5	76
1.5	14.5	0.1	78.5	57.2	145
		0.125	81.6	60.3	116
		0.15	**84.7**	**63.4**	**97.5**
		0.175	82.9	61.1	82.8

		0.15	71.5	53.3	130
2.0	19.5	0.175	75.6	57.4	111.4
		0.2	**79.3**	**60.1**	**97.5**
		0.225	74.2	56.2	66.6
2.5	24.5	0.2	69.2	50.1	122.5
		0.225	72.5	53.2	108.8
		0.25	**76.5**	**56.3**	**98**
		0.275	73.1	54.8	89.0

The degradation and mineralization increased with increase in OH radical production (Rivas et al., 2002; Yilmaz et al., 2010). At higher concentration of Fe^{2+} concentration the 3-NA removal and COD removals were less due to the ferrous ion inhibition that occurs when a high concentration of Fe^{2+} is present in the system and Fe^{2+} itself can react with OH radicals resulting in the scavenging of OH radical (Hsueh et al., 2005). This may be due to refractory intermediates formed during the treatment.

For higher concentration of 3-NA, viz.1.0, 1.5, 2.0 and 2.5mM Fe dosages were optimized in similar way. The optimized iron concentrations were 0.05, 0.1, 0.15, 0.2, 0.25mM for respectively for 0.5, 1.0, 1.5, 2.0 and 2.5mM respectively.

Optimum Fenton's dosage for each initial concentration of 3-NA and the corresponding 3-NA removal and COD removal obtained were summarized in Table 4.6.

Table 4.6: Optimum dosages obtained during Fenton's oxidation of 3-NA

Initial 3-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} Concentration (mM)	3-NA removal (%)	COD removal (%)	H/F ratio
0.5	4.5	0.05	88.7	71.7	90
1.0	9.5	0.1	86.9	66.4	95
1.5	14.5	0.15	84.7	63.4	96.6
2.0	19.5	0.2	79.3	60.1	97.5
2.5	24.5	0.25	76.5	56.3	98

The degradation of 3-NA is supported by UV-VIS absorbance spectrum of 3-NA before and after treatment. The UV-VIS absorbance peak is 279nm before treatment and is disappeared after treatment (Figure.A5) Indicating the degradation of 3-Nitroaniline.

The HPLC analysis was carried out for the 3-NA concentrations of 0.5-2.5mM concentration at an optimum dosage. The chromatograph for 3-NA before and after treatment are shown in Figure A15 & A16. The retention time obtained 3-NA was 6.1 minutes, whereas, after Fenton's treatment under optimum conditions, the chromatograph obtained is as shown in Figure A16. This confirms the experimental results reported earlier.

4.1.3 Fenton oxidation of 4-Nitroaniline

4.1.3.1 Effect of pH

In order to find the optimal pH for the degradation of 4-Nitroaniline, Fenton's oxidation experiments were conducted at different pH in the range of 2 to 4 with an initial concentration of 0.5 mM. Figure 4.7 shows the 4-NA and COD removal efficiencies of the initial concentration of 0.5mM at different pH keeping the ratio of H_2O_2: Fe^{2+}:: 3.5: 0.05. The removal of 4-NA was maximum at pH 3 compared to all other pH values between 2 to 4. The maximum 4-NA removal of 86.5% and COD removal of 76.3% was obtained at pH 3. At pH 2, 2.5, 3.5 and 4, removal efficiencies were less than at optimum value.
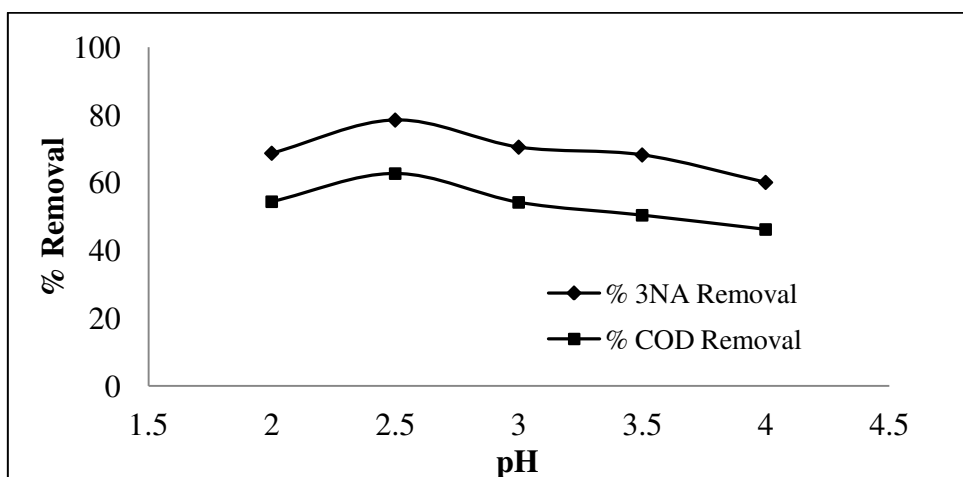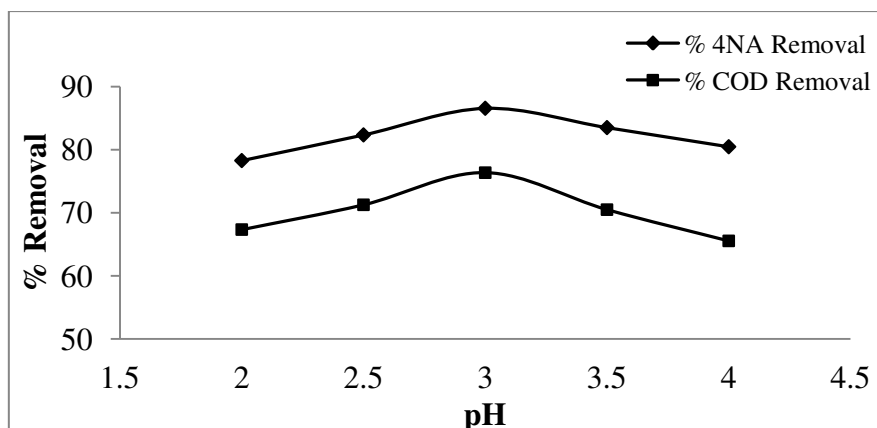
Figure 4.7: Effect of pH on removal of 4-Nitroaniline (4-NA concentration: 0.5 mM, H$_2$O$_2$ dosage: 3.5 mM, Fe dosage: 0.05 mM, Reaction time = 5hrs)

4.1.3.2 Effect of H$_2$O$_2$ Concentration

The amount of hydrogen peroxide is an important parameter that influences the Fenton's oxidation process. Figure 4.8 shows the 4-NA and COD removal efficiencies for 0.5mM of 4-NA concentration as a function of H$_2$O$_2$ concentration. For 0.5mM 4-NA concentration, the H$_2$O$_2$ concentration was varied from 4.0-5.5mM keeping Fe concentration constant as 0.05mM, maximum removal of 99.8% and COD removal of 86.2% was obtained at 5.0mM H$_2$O$_2$. When the H$_2$O$_2$ concentration was 4.0mM, the removal was found to be 93.6% and 79.7% for 4-NA and COD respectively. Next, the H$_2$O$_2$ concentration was increased to 4.5mM and removal efficiencies obtained was 95.1% and 82.6% respectively for 4-NA and COD removal. Further study was carried out for 5.5mM of H$_2$O$_2$ concentration. The removal efficiency obtained for 5.5mM of H$_2$O$_2$ concentration are 96.5% and 83.7% for 4-NA and COD removal respectively. The maximum removal of 99.8% and COD removal of 86.2% was obtained at 5.0mM H$_2$O$_2$. As the H$_2$O$_2$ concentration increased to 5.5mM, the 4-NA and COD removal was decreased.
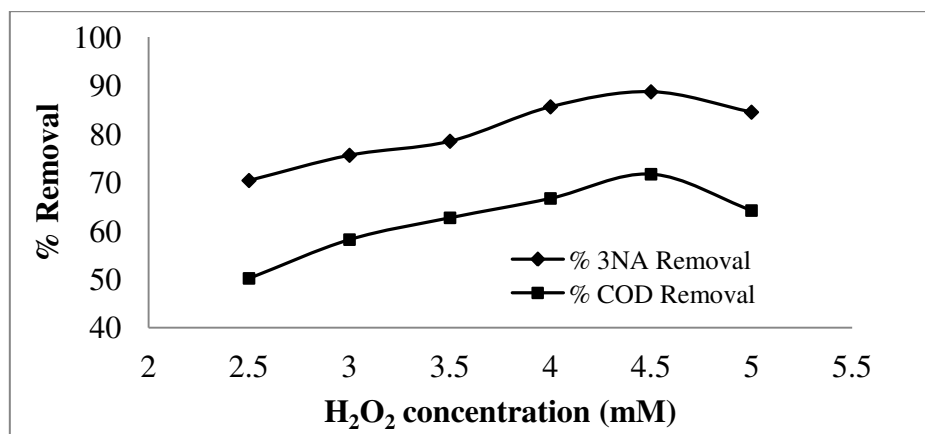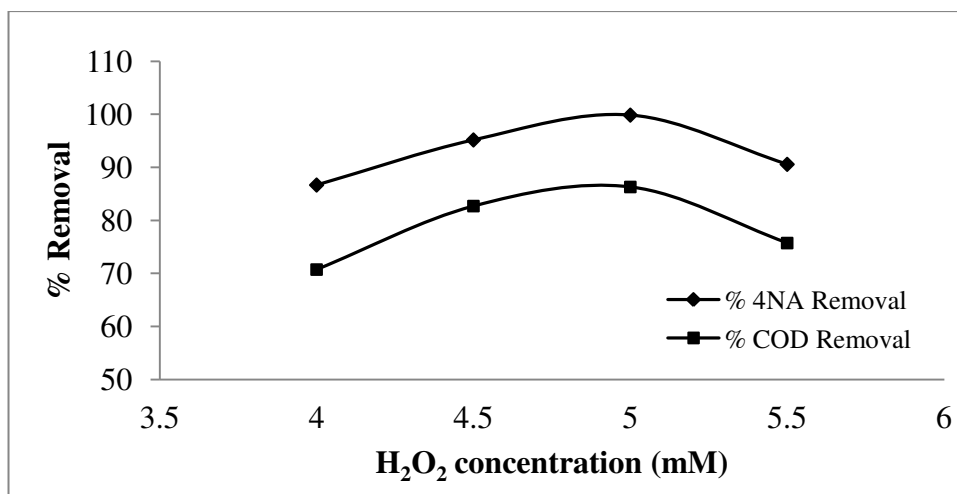
Figure 4.8: Effect of H₂O₂ concentration on removal of 4-Nitroaniline (4NA concentration: 0.5mM, Fe dosage: 0.05mM, pH = 3.0, Reaction Time =5hrs)

Similarly, for 1mM of 4NA, H_2O_2 concentration was varied from 5.5-11mM and maximum 4-NA removal of 98.2 % and COD removal of 84.6 % was observed at 10.5mM mm at Fe concentration of 0.1mM. Then for 1.5mM concentration, the H_2O_2 concentration was varied from 11.0 mM to 16.5mM, Fe concentration was kept constant as 0.15mM. The maximum removal of 96.4 % and COD removal of 82.7% was obtained at H_2O_2 concentration of 16.0mM. For the 2.0mM of 4-NA concentration, the hydrogen peroxide dosage was varied from 16.5mM-22.0mM keeping Fe concentration as 0.2mM. The maximum removal of 94.6 % and COD removal of 80.1 % was obtained at 21.5mM of H_2O_2 concentration. Further for 2.5mM of 4-NA concentration, the H_2O_2 concentration was varied from 22.0-27.5mM and Fe concentration was kept constant as 0.25mM. The maximum 4-NA removal and COD removal obtained was 93.7% and 79.3% respectively at H_2O_2 concentration of 27.0mM. All the experiments were carried out for a reaction period. Residual H_2O_2 was negligible after the reaction period. Table 4.7 provides the maximum 4-NA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration. The optimized hydrogen peroxide dosages for 0.5, 1, 1.5, 2, 2.5mM of 4-NA concentration were 5, 10.5, 16, 21.5 and 27mM respectively.

Table 4.7: Effect of H_2O_2 concentration on different initial concentration of 4-NA at constant Fe $^{2+}$ dosage

4-NA (mM)	Fe^{2+} (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	4	93.6	79.7	80
		4.5	95.1	82.6	90
		5	**99.8**	**86.2**	**100**
		5.5	96.5	83.7	110
1.0	0.1	5.5	83.2	65.6	55
		6.0	84.8	67.7	60
		6.5	86.5	69.4	65
		7.0	88.6	70.5	70
		7.5	89.7	72.1	75
		8.0	91.2	74.7	80
		8.5	92.4	75.5	85
		9.0	93.9	77.2	90
		9.5	94.2	80.6	95
		10.0	96.4	82.9	100
		10.5	**98.2**	**84.6**	**105**
		11.0	94.8	80	110
1.5	0.15	11.0	81.6	64.9	73.3
		11.5	83.3	66.3	76.6
		12.0	85.4	68.1	80
		12.5	86.9	69.5	83.3
		13.0	88.1	71.9	86.6
		13.5	89.5	73.6	90
		14.0	91	75.2	93.3
		14.5	92.1	77.5	96.6
		15.0	93.3	78	100
		15.5	95.1	80	103.3
		16.0	**96.4**	**82.7**	**106.6**
		16.5	94.2	80.5	110

|		16.5	79.1	65.5	82.5
		17.0	81.4	67.6	85
		17.5	82.3	69.1	87.5
		18.0	84.5	70.4	90
		18.5	85.6	70.7	92.5
2.0	0.2	19.0	86.2	71.3	95
		19.5	87.5	72.5	97.5
		20.0	89.7	74.9	100
		20.5	90.1	76.2	102.5
		21.0	92.7	77.9	105
		21.5	**94.6**	**80.1**	**107.5**
		22.0	91.4	76.7	110
		22.0	77.4	62	88
		22.5	78.6	65.2	90
		23.0	80.2	67.6	92
		23.5	81.3	69.5	94
		24.0	83.5	70.8	96
2.5	0.25	24.5	85.0	71.7	98
		25.0	87.6	73.6	100
		25.5	88.9	75.8	102
		26.0	90.7	76.6	104
		26.5	92.4	78.3	106
		27.0	**93.7**	**79.3**	**108**
		27.5	90.1	77.5	110
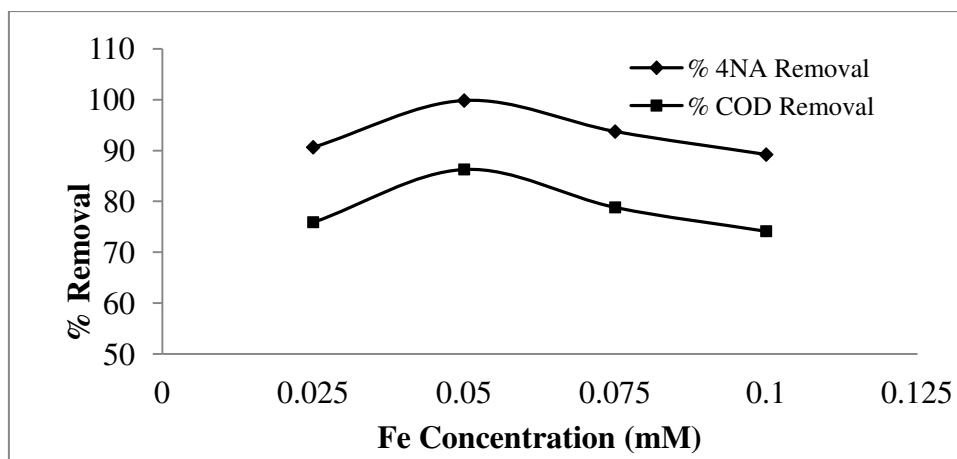
Figure 4.9: Effect of Fe concentration on removal of 4-Nitroaniline (4-NA concentration: 0.5mM, H_2O_2 dosage: 5.0mM, pH = 3.0, Reaction Time =5hrs)

4.1.3.2 Effect of Fe^{2+} Concentration

After the H_2O_2 dosages were optimized, the iron dosages were varied and optimized. The Fe concentration was varied from 0.025-0.1mM at an interval of 0.025mM for the initial concentration of 0.5mM keeping H_2O_2 dosage constant as 5.0mM. The experiments were conducted at previously optimized hydrogen peroxide concentration. The maximum removal of 99.8% and COD removal of 86.2% was obtained at 0.05mM Fe concentration. When the Fe concentration was 0.025mM, the 4-NA removal was 95.6% and COD removal was 81.9%. The maximum removal efficiencies were obtained at Fe concentration of 0.05mM i.e. 99.8% of 4-NA and COD removal of 86.2%. Then the removal efficiencies were decreased to 97.7% and 80.8% respectively for 4-NA and COD at Fe concentration of 0.075mM. Further increase in the Fe concentration of 0.1mM, the 4-NA and COD removal efficiencies obtained were 93.2 % and 78.1% respectively are as shown in Figure 4.9. Hence the optimized iron concentration was 0.05mM for 0.5mM of 4-NA concentration.

Similarly, studies were conducted for different initial concentrations of 4-NA. For 1.0mM of 4-NA, Fe concentration varied from 0.05-0.125mM and maximum removal of 98.2% and COD removal of 84.6% was obtained at 0.1mM of Fe concentration. Then for 1.5mM of 4-NA concentration, Fe concentration varied from 0.1-0.175mM and optimized Fe concentration was 0.15mM. The maximum removal

of 96.4% and COD removal of 82.7% obtained. Then the initial concentration of 4-NA is increased to 2.0mM and Fe concentration varied from 0.15mM-0.225mM, the maximum 4-NA removal of 94.6% and 79.1% COD removal was obtained at Fe concentration of 0.2mM. Then for 2.5mM initial concentration of 4-NA, Fe concentration is varied from 0.2-0.275mM. The maximum 4-NA removal and COD removal of 93.7% and 80.3% respectively were achieved at 0.25mM of Fe concentration at optimized hydrogen peroxide concentration of 27.0mM. When the concentration of Fe^{2+} was higher, a great amount of Fe^{3+} from the process of H_2O_2 decomposition by Fe^{2+} was easy to exit in the form of $Fe(OH)^{2+}$ in the acidic environment. As it can be seen, the effect of increasing H_2O_2 was first positive for the degradation of 4-NA. This is due to the oxidation power of Fenton's process which improved with increasing OH radical in the solution obtained from the decomposition of increasing hydrogen peroxide. Table 4.8 presents the results of 4-NA and COD removal efficiencies as a function of Fe^{2+} concentration at a different initial concentration at constant H_2O_2. The optimum iron dosages obtained were 0.05, 0.1, 0.15, 0.2 and 0.25mM for the 4-NA concentrations of 0.5, 1, 1.5, 2.0 and 2.5mM respectively.

Table 4.8: Effect of Fe $^{2+}$ concentration on different initial concentration of 4-NA at constant H_2O_2 dosage

4-NA (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	% Removal	% COD removal	H/F ratio
0.5	5	0.025	95.6	81.9	200
		0.05	**99.8**	**86.2**	**100**
		0.075	97.7	80.8	66.7
		0.1	93.2	78.1	50
1	10.5	0.05	90.0	79.9	210.0
		0.075	93.1	80.9	140.0
		0.1	**98.2**	**84.6**	**105**
		0.125	95.5	81.7	84.0
1.5	16	0.1	93.0	77.5	160.0

		0.125	94.1	80.1	128.0
		0.15	**96.4**	**82.7**	**106.6**
		0.175	93.9	79.5	91.4
2.0	21.5	0.15	90.8	73.1	143.3
		0.175	92.3	77.5	122.8
		0.2	**94.6**	**79.1**	**107.5**
		0.225	91.6	76.4	95.5
2.5	27	0.2	87.3	73.2	135.0
		0.225	90.7	75.3	120.0
		0.25	**93.7**	**80.3**	**108.0**
		0.275	91.4	78.1	98.1

The optimum Fenton's dosages for initial concentrations varying from 0.5-2.5mM of 4-NA and the respective 4-NA removal and COD removal are summarized in Table 4.9.

Table 4.9: Optimum dosages obtained during Fenton's oxidation of 4-Nitroaniline

Initial 4-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} concentration (mM)	4-NA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	99.8	86.2	100
1.0	10.5	0.1	98.2	84.6	105
1.5	16.0	0.15	96.4	82.7	106.6
2.0	21.5	0.2	94.6	80.1	107.5
2.5	27.0	0.25	93.7	79.3	108

The degradation of 4-Nitroaniline can be well supported by comparing the UV-VIS spectrum of the sample before and after treatment. The UV-VIS spectrum obtained before treatment has a peak at 380nm in UV region as seen in the figure. (A10). But, in the UV-VIS spectrum of treated sample, a peak at 380nm has

disappeared, indicating the degradation of 4-Nitroaniline in Fenton's oxidation. This also confirms the results of the previous set of experiments.

The HPLC analysis was carried for the 4-NA for 0.5mM concentration at an optimum dosage. The chromatograph for the 0.5mM 4-NA before and after treatment are shown in Figure A17 & A18. The retention time obtained 4-NA is 1.6 minutes as shown in Figure A17, whereas, after Fenton's treatment under optimum conditions, the chromatograph obtained is as shown in Figure A18 and it indicates that, no peak was observed at a retention time of 1.6 minutes i.e. the 4-NA is degraded completely. This confirms the experimental results reported earlier.

4.1.4 Fenton oxidation of 2-Methoxyaniline

4.1.4.1 Effect of pH

The pH was optimized for 2-Methoxyaniline by varying the pH in the range of 2-4 at an interval of 0.5, keeping the ratio of H_2O_2: Fe^{2+}:: 3.5:0.05. The maximum removal efficiency was observed at pH 3. The maximum removal efficiencies obtained at pH 3 were 81.4% and 69.7 % respectively for 2-MA and COD removal. The removal efficiencies obtained at different pH values are as shown in Figure 4.10. Hence the optimum pH obtained for 2-MA was 3.
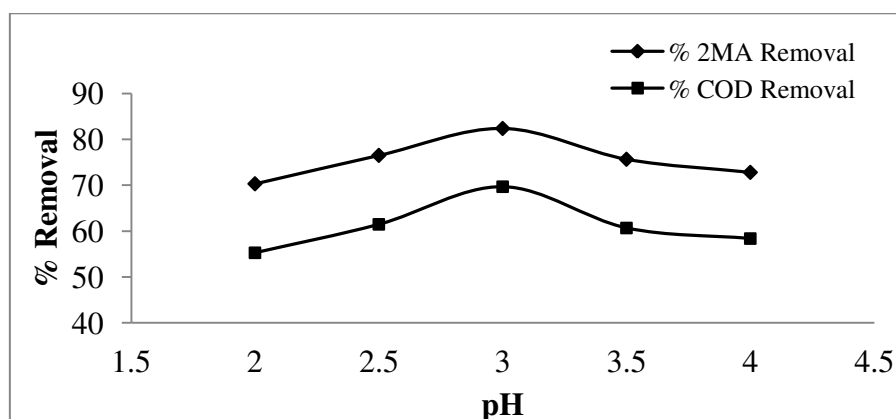
Figure 4.10: Effect of pH on removal of 2-Methoxyaniline (2-MA concentration: 0.5mM, H_2O_2 dosage: 3.5mM, Fe dosage: 0.05mM, Reaction time = 5hrs)

4.1.4.2 Effect of H$_2$O$_2$ Concentration

The concentration of hydrogen peroxide is one of the important parameters to influence the Fenton's oxidation. Initially, hydrogen peroxide concentration was optimized for 0.5mM initial concentration of 2-MA, experiments were carried out by varying the H$_2$O$_2$ concentration from 2.5-4.5mM at pH 3.0 by keeping iron concentration constant as 0.05mM. The maximum 2-MA and COD removal were 82.4 % and 69.7% respectively at 3.5mM of H$_2$O$_2$ concentration. When H$_2$O$_2$ concentration was 2.5mM, the 2-MA removal and COD removal was found to be 74.2% and 60.3%. As the H$_2$O2 concentration increased from 3.0mM to 3.5mM, the removal of 2-MA and COD has increased from 77.3% to 82.4% and 65.6% to 69.7%. When the H$_2$O$_2$ concentration was 4.0mM, the less removal of 75.2% and 64.6% of 2-MA and COD were observed. Further increase in the hydrogen peroxide concentration to 4.5mM, the 2-MA and COD removal efficiencies obtained were 68.4 % and 57.2% respectively which is as shown in Figure 4.11. This is because of the decreased catalytic activity with increased H$_2$O$_2$ concentration. Also with the increases in the H$_2$O$_2$ concentration from 3.5mM to 4.0mM, the degradation rate of 2-MA decreased. This may be explained by the fact that the very reactive OH radical could be consumed by H$_2$O$_2$ and results in the generation of less reactive OOH radical (Kang et al., 2002, Walling, 1975). Table 4.10 provides the maximum 2-MA removal and COD removal efficiencies obtained as a function of initial concentration at different H$_2$O$_2$ concentration.
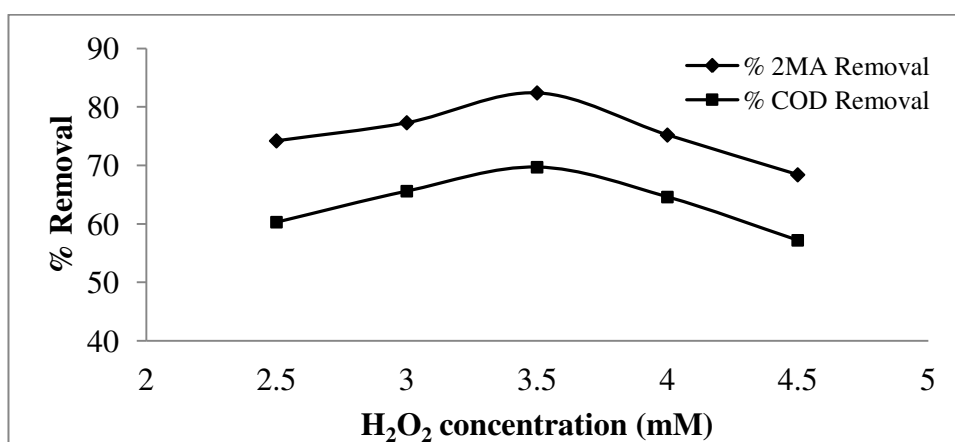
Figure 4.11: Effect of H$_2$O$_2$ concentration on removal of 2-Methoxyaniline (2-MA concentration: 0.5mM, Fe dosage: 0.05mM, pH = 3.0, Reaction Time =5hrs)

The hydrogen peroxide concentration was further optimized for a higher concentration of 2-MA. For 1mM of 2-MA concentration, H_2O_2 dosage was varied in the range of 4.5-8mM. Similarly for 1.5mM, 8-12mM, for 2.0mM, 12-16mM and for 2.5 mM, 16-20mM. The optimized hydrogen peroxide dosages for the 0.5, 1, 1.5, 2, 2.5mM of 2-MA concentration were 3.5, 7.5, 11.5, 15.5 and 19.5 respectively.

Table 4.10: Effect of H_2O_2 concentration on different initial concentration of 2-MA at constant Fe^{2+} dosage

2-MA (mM)	Fe^{2+} (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	2.5	74.2	60.3	50
		3	77.3	65.6	60
		3.5	**82.4**	**69.7**	**70**
		4	75.2	64.6	80
		4.5	68.4	57.2	90
1.0	0.1	4.5	60.2	49.8	45
		5	63.6	51.3	50
		5.5	66.5	54.5	55
		6	69.2	56.8	60
		6.5	73.5	60.8	65
		7	77.2	64.6	70
		7.5	**79.9**	**67.9**	**75**
		8	75.5	58.5	80
1.5	0.15	8	58.1	43.7	53.4
		8.5	60.2	46.6	56.7
		9	62.3	48.3	60
		9.5	65.8	51.9	63.3
		10	67.7	54.9	66.6
		10.5	70.8	56.2	70
		11	74.2	60.1	73.3
		11.5	**76.8**	**62.2**	**76.6**

		12	73.5	60.1	80
2.0	0.2	12	53.6	40.2	60
		12.5	57.2	43.7	62.5
		13	60.7	46.6	65
		13.5	63.2	50.4	67.5
		14	66.7	52.7	70
		14.5	67.8	55.3	72.5
		15	71.5	57.5	75
		15.5	**73.1**	**59.4**	**77.5**
		16	70.2	56.1	80
2.5	0.25	16	52.8	38.2	64
		16.5	55.7	40.3	66
		17	57.3	43.7	68
		17.5	60.6	46.4	70
		18	62.2	48.6	72
		18.5	65.3	50.8	74
		19	67.5	53.2	76
		19.5	**69.6**	**55**	**78**
		20	66.4	52.7	80

4.1.4.3 Effect of Fe^{2+} Concentration

After H_2O_2 dosage was optimized, the optimization of iron dosage was carried out by varying iron concentration. The iron concentration was varied from 0.025mM-0.125mM keeping the H_2O_2 concentration constant as 3.5mM for the 2-MA concentration of 0.5mM. For an initial Fe^{2+} concentration of 0.025mM, removal of 2-MA was 76.2% and COD removal was 65.8% and for the iron concentration of 0.05mM, removal was found to be 82.4% and 69.7% respectively for 2-MA and COD. For 0.075mM the degradation of 2-MA decreased to 78.5% and COD removal to 64.2%. In the case of Fe^{2+} concentration of 0.1mM, the 2-MA and COD removal efficiencies decreased to 74.6% and 60.5% respectively. Maximum removal obtained at 0.05mM of Fe^{2+} concentration and optimum 2-MA and COD removal were observed to be 82.4% and 69.7% respectively as shown in Figure 4.12. Hence the

optimum iron dosage for 0.5mM concentration of 2-MA was 0.05mM. When the concentration of Fe^{2+} was higher, it has been reported in the literature, there is a possible Ferric sludge generation leading to lower degradation. For a higher concentration of 2-MA, the iron dosages were optimized for a higher concentration of 2-MA. The optimized iron dosages obtained for 1, 1.5, 2.0 and 2.5mM of 2-MA concentrations were 0.1, 0.15, 0.2 and 0.25mM.

When the initial concentration of 2-MA was increased the degradation rate of 2-MA decreased as a result of scavenging effect. H_2O_2 and iron dosages were optimized in a similar way as explained in the previous section. For the next set of experiments, an optimum dosage from previous concentration were chosen as starting dosages and then increased gradually to find the optimum. For higher concentration of pollutant, more hydrogen peroxide is consumed while iron dosage increased in usual order, the trend which was observed in 2-MA. It is clear from the results that as the initial concentration of 2-MA increased the removal of pollutant got decreased. Also, there was a gradual increase in Fenton's dosages as we increase the initial pollutant concentration. This can be supported by the literature, where COD removal of model compounds by Fenton oxidation is more for the lower initial concentration of the compounds (Yilmaz et al., 2010).

Figure 4.12: Effect of Fe concentration on removal of 2-Methoxyaniline (2-MA concentration: 0.5mM, H_2O_2 dosage: 3.5mM, pH = 3.0, Reaction Time =24hrs)

Table 4.10 presents the results of 2-MA and COD removal efficiencies as a function of Fe^{2+} concentration at a different initial concentration at constant H_2O_2. The optimized dosage obtained for different concentration of 2-MA are tabulated in Table 4.11.

Table 4.11: Effect of Fe^{2+} concentration on different initial concentration of 2-MA at constant H_2O_2 dosage

2-MA (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	% Removal	% COD removal	H/F ratio
0.5	3.5	0.025	76.2	65.8	140
		0.05	**82.4**	**69.7**	**70**
		0.075	78.5	64.2	46.7
		0.1	74.6	60.5	35
1	7.5	0.05	72.2	60.7	150
		0.075	76.5	64.8	100
		0.1	**79.9**	**67.9**	**75**
		0.125	75.2	63.8	60
1.5	11.5	0.1	70.3	56.3	115
		0.125	74.1	60.5	92
		0.15	**76.8**	**62.2**	**76.7**
		0.175	73.7	58.7	65.7
2.0	15.5	0.15	68.7	54.2	103.4
		0.175	71.6	57.6	88.5
		0.2	**73.1**	**59.40**	**77.5**
		0.225	70.2	55.7	68.9
2.5	19.5	0.2	61.5	48.2	97.5
		0.225	64.2	52.3	86.7
		0.25	**69.6**	**55**	**78**
		0.275	65.6	53.7	70.9

Table 4.12: Optimum dosages obtained during Fenton's oxidation of 2-Methoxyaniline

Initial 2-MA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} concentration (mM)	2-MA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	82.4	69.7	70
1.0	7.5	0.1	79.9	67.9	75
1.5	11.5	0.15	76.8	62.2	76.6
2.0	15.5	0.2	73.1	59.4	77.5
2.5	19.5	0.225	69.6	55	78

The degradation of 2-Methoxyaniline is justified by UV-VIS spectra of 2-Methoxyaniline derived before and after treatment. The peak was observed at 282.5nm for the compound and which is disappeared in the spectra after treatment, indicating degradation (Figure A.10).

The HPLC analysis was carried out for 2-MA for the concentrations varying from 0.5-2.5mM. The Figure A19 & A20 shows the HPLC chromatograph of 2.5mM of 2-MA concentration before and after treatment. The retention time obtained for 2-MA was 1.4 minutes as shown in Figure A19 whereas after treatment at optimum conditions the no peak was observed at the retention time of 1.4 minutes. This chromatograph confirms the experimental results obtained earlier.

4.1.5. Fenton oxidation of 4-Methoxyaniline

4.1.5.1 Effect of pH

The pH was optimized by varying the pH in the range of 2-4 keeping the ratio of H_2O_2: Fe^{2+}:: 3.5: 0.05. Figure 4.13 explains the effect of pH on 4-MA removal. The maximum removal obtained was pH 2.5. The maximum 4-MA removal of 70.8% and COD removal of 58.6 % was observed.
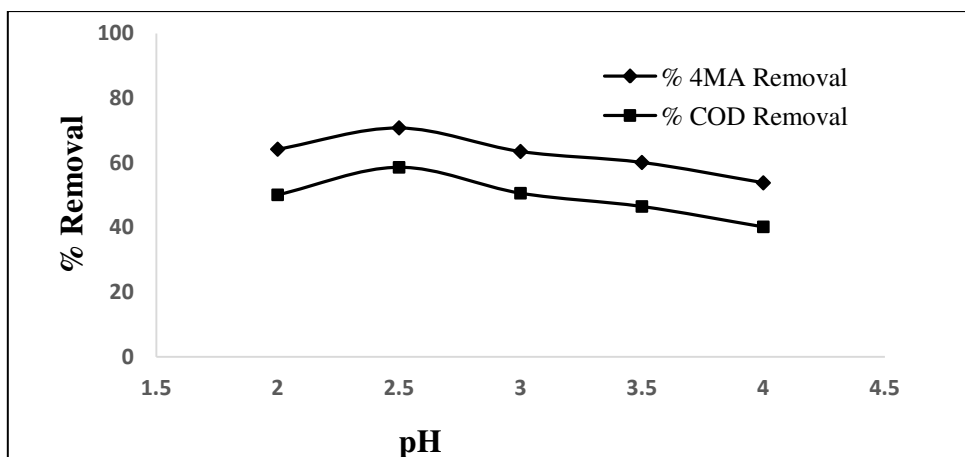
Figure 4.13: Effect of pH on removal of 4-Methoxyaniline (4-MA concentration: 0.5mM, H₂O₂ dosage: 3.5mM, Fe dosage: 0.05mM, Reaction Time =5hrs)

4.1.5.2 Effect of H_2O_2 Concentration

The concentration of hydrogen peroxide is one of the important parameters to influence the Fenton's oxidation. Initially, Fenton's dosages were optimized for 0.5mM initial concentration of 4-MA, experiments were carried out by varying the H_2O_2 concentration from 3.5-5.5mM at pH 2.5 by keeping iron concentration constant at 0.05mM. The maximum 4-MA and COD removal were 85.5 % and 71.1% respectively at 5.0mM of H_2O_2 concentration. When H_2O_2 concentration was 3.5mM, the 4-MA removal and COD removal was found to be 70.8% and 58.6%. As the H_2O_2 concentration was increased from 4.0 to 4.5mM, the removal of 4-MA and COD has increased from 75.6% to 80.4% and 63.2% to 67.5%. When the H_2O_2 concentration was 5.0 mM, the maximum 4-MA and COD removal of 85.5% and 71.1% respectively were observed. For 5.5 mM of H_2O_2 concentration, removal efficiency decreased to 79.2% and 66.7% for 4-MA and COD respectively as shown in Figure 4.14. Studies were further carried out for higher concentrations of 4-MA and the results obtained are tabulated in Table 4.13. The optimized H_2O_2 dosages obtained for 0.5, 1, 1.5, 2 and 2.5 mM of 4-MA concentration were 5, 10.5, 16, 21.5 and 27mM respectively. This is because of the decreased catalytic activity with increased H_2O_2 concentration. Also with the increase in the H_2O_2 concentration from 5.0mM to 5.5mM, the degradation rate of 4-MA decreased. This may be explained by the fact

that the very reactive OH radical could be consumed by H_2O_2 and results in the generation of less reactive OOH radical (Kang et al., 2002, Walling and Kato, 1971). Table 4.13 provides the 4MA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration.
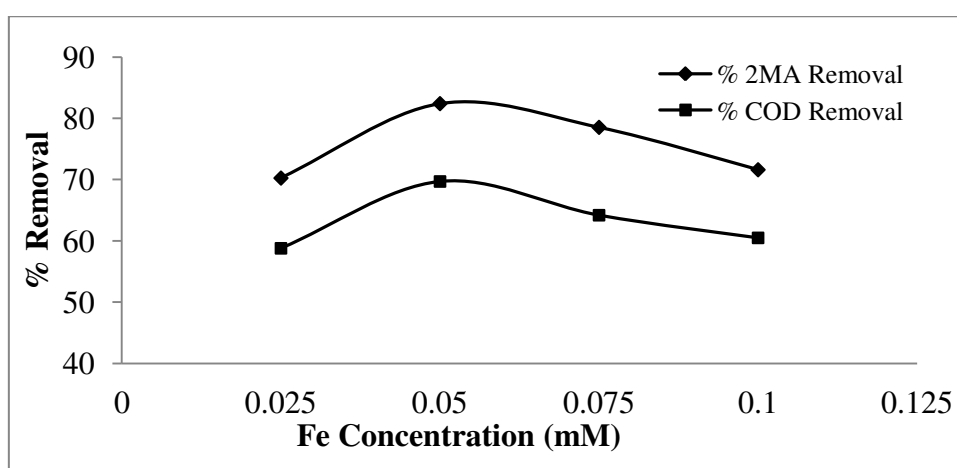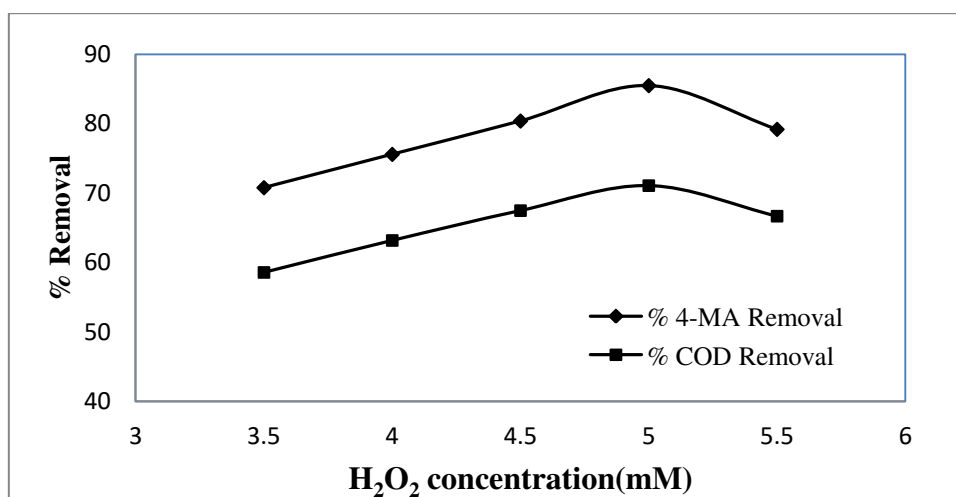

Figure 4.14: Effect of H_2O_2 concentration on removal of 4-Methoxyaniline (4MA concentration: 0.5mM, Fe dosage: 0.05mM, pH = 2.5, Reaction Time =5hrs)

Table 4.13: Effect of H_2O_2 concentration on different initial concentration of 4-MA at constant Fe^{2+} dosage

4-MA (mM)	Fe^{2+} (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	3.5	70.8	58.6	70
		4.0	75.6	63.2	80
		4.5	80.4	67.5	90
		5.0	**85.5**	**71.1**	**100**
		5.5	79.2	66.7	110
1.0	0.1	5.5	59.5	43.6	55
		6.0	62.7	48.5	60
		6.5	64.8	49.9	65
		7.0	68.5	53.4	70

		7.5	70.3	56.2	75
		8.0	72.4	59.4	80
		8.5	75.7	60.7	85
		9.0	77.6	64.6	90
		9.5	79.3	66.3	95
		10.0	81.5	67.4	100
		10.5	**83.4**	**68.3**	**105**
		11.0	79.7	65.4	110
		11.0	55.6	41.6	73.3
		11.5	57.2	42.5	76.6
		12.0	59.5	44.3	80
		12.5	61.3	47.5	83.3
		13.0	63.7	50.7	86.6
1.5	0.15	13.5	65.5	52.8	90
		14.0	68.7	53.9	93.3
		14.5	70.5	56.6	96.6
		15.0	75.6	60.6	100
		15.5	78.2	63.5	103.3
		16.0	**81.5**	**66.8**	**106.6**
		16.5	77.6	62.7	110
		16.5	54.5	38.7	10
		17.0	56.2	41.6	85
		17.5	59.4	44.5	87.5
		18.0	60.8	46.5	90
		18.5	63.7	47.6	92.5
		19.0	65.5	50.1	95
2.0	0.2	19.5	66.7	51.7	97.5
		20.0	68.8	54.5	100
		20.5	70.3	55.3	102.5
		21.0	73.3	59.1	105
		21.5	**76.7**	**60.2**	**107.5**
		22.0	71.6	57.5	110

		22.0	45.2	32.5	88
		22.5	47.6	33.4	90
		23.0	49.8	35.4	92
		23.5	52.5	38.1	94
		24.0	54.7	39.7	96
2.5	0.25	24.5	56.4	42.7	98
		25.0	59.7	46.7	100
		25.5	61.5	48.3	102
		26.0	65.6	51.4	104
		26.5	67.7	53.8	106
		27.0	**72.3**	**58.8**	**108**
		27.5	66.5	50.7	110

4.1.5.3 Effect of Fe^{2+} Concentration

The optimization of iron dosage is carried out by varying iron concentration from 0.025mM-0.1mM keeping the H_2O_2 concentration constant as 5.0mM for the pollutant dosage of 0.5mM. Maximum removal was obtained at 0.05mM of Fe^{2+} concentration and 4-MA and COD removal were observed to be 85.5% and 71.1% respectively as shown in Figure 4.15. For initial Fe^{2+} concentration of 0.025mM, removal of 4-MA was 78.3% COD removal was 65.2% and for 0.05mM of Fe^{2+}concentratio, removal was found to be 85.5% and 71.1% respectively for 4-MA and COD. As the Fe^{2+} concentration increased from 0.025mM to 0.05mM removal efficiency was increased. When the iron concentration increased to 0.075mM the removal efficiency decreased to 76.4% and 60.5% respectively for 4-MA and COD. Further increase in the iron concentration to 0.1mM, the removal efficiency decreased further to 70.5 % and 58.5% respectively for 4-MA and COD. Iron dosages were optimized in a similar way as explained in the previous section. For the next set of experiments, optimum dosages of previous concentration was chosen as a starting dosage and then increased gradually to find the optimum. Hence the optimum iron dosages obtained for 1, 1.5, 2.0 and 2.5mM of 2-MA concentration were 0.1, 0.15, 0.2 and 0.25mM respectively. Table 4.14 presents the results of 4-MA and COD removal

efficiencies as a function of Fe^{2+} concentration at a different initial concentration at constant H_2O_2.

When the concentration of Fe^{2+} was higher, a great amount of Fe^{2+} from the process of H_2O_2 decomposition by Fe^{2+} was easy to exit in the form of $Fe\ (OH)^{2+}$ in an acidic environment, which resulted in low degradation. When the initial concentration of 4-MA was increased the degradation rate of 4-MA decreased as a result of scavenging effect.
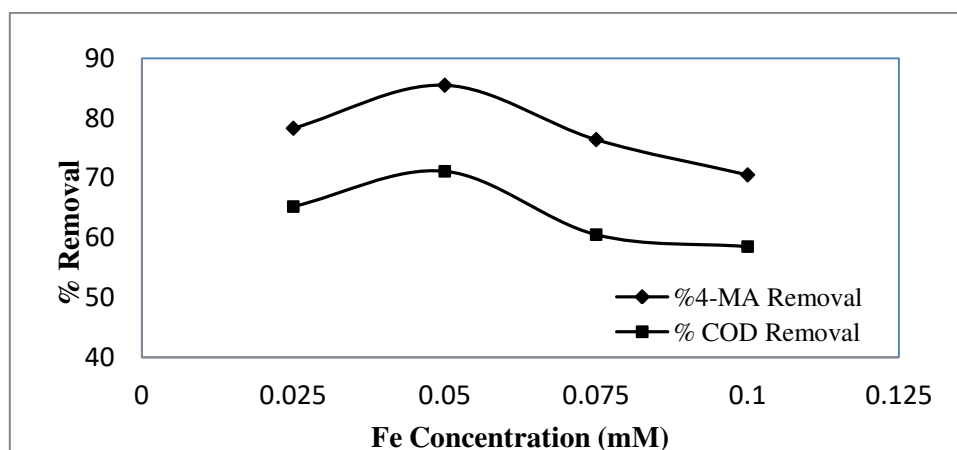
Figure 4.15: Effect of Fe concentration on removal of 4-Methoxyaniline (4MA concentration: 0.5mM, H_2O_2 dosage: 5.0mM, pH = 2.5, Reaction Time =5hrs)

Table 4.14: Effect of Fe $^{2+}$ concentration on different initial concentration of 4-MA at constant H_2O_2 dosage

4-MA (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	% Removal	% COD removal	H/F ratio
0.5	5.0	0.025	78.3	65.2	200
		0.05	**85.5**	**71.1**	**100**
		0.075	76.4	60.5	66.6
		0.1	70.5	58.5	50
1	10.5	0.05	70.3	57.8	210
		0.075	78.8	63.6	140
		0.1	**83.4**	**68.3**	**105**

		0.125	75.5	60.8	84
1.5	16.0	0.1	70.2	54.5	160
		0.125	76.5	62.4	128
		0.15	**81.5**	**66.8**	**106.6**
		0.175	75.7	58.5	91.4
2.0	21.5	0.15	64.8	50.2	143.3
		0.175	70.6	55.7	122.8
		0.2	**76.7**	**60.2**	**107.5**
		0.225	68.7	53.4	95.5
2.5	27.0	0.2	60.8	45.6	135
		0.225	66.5	50.7	120
		0.25	**72.3**	**58.8**	**108**
		0.275	64.2	49.7	98.1

It is clear from the results that as the initial concentration of 4-MA increased the removal of pollutant got decreased. Also, there was a gradual increase in Fenton's dosages as we increase the initial pollutant concentration. This can be supported by the literature, where COD removal of model compounds by Fenton oxidation is more for the lower initial concentration of the compounds (Yilmaz et al., 2010).

For higher concentration of 4-MA, viz.1.0, 1.5, 2.0 and 2.5mM hydrogen peroxide and Fe dosages were optimized. Optimum Fenton's dosage for each initial concentration of 4-MA and the respective % 4-MA removal and % COD removal are summarized in Table 4.15.

Table 4.15: Optimum dosages obtained during Fenton's oxidation of 4-Methoxyaniline

Initial 4-MA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} concentration (mM)	4-MA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	90.6	76.8	100
1.0	10.5	0.1	87.5	72.3	105

1.5	16.0	0.15	84.3	70.5	106.6
2.0	21.5	0.2	80.5	64.7	107.5
2.5	27.0	0.25	76.5	62.3	108

The degradation of 4-Methoxyaniline is justified by UV-VIS spectra of 4-Methoxyaniline derived before and after treatment. The peak was observed at 296nm for the compound and which is disappeared in the spectra after treatment, indicating degradation (Figure.A12).

The HPLC analysis was carried for the 4-MA for varying initial concentration at an optimum dosage. The retention time obtained for 4-MA was 1.3 minutes as shown in Figure A21. Whereas, after Fenton's treatment under optimum condition, the chromatograph obtained was shown in Figure A22 and it indicates that, no peak was observed at a retention time of 1.3 minutes i.e. the 4-MA was degraded completely. This confirms the experimental results.

4.1.6 Fenton oxidation of 2-Nitroaniline using laterite iron as a catalyst

The Fenton experiments were carried out using $FeSO_4$ as an iron source and to reduce the cost, iron from locally available laterite soil was used. The experimental results are presented below.

4.1.6.1 Effect of H_2O_2 Concentration

The Fenton's oxidation has been carried for 2-Nitroaniline using iron extracted from laterite soil as a source of iron. The experiments were carried out by varying H_2O_2 and iron concentration. Initially, for 0.5mM of 2-NA concentration, the H_2O_2 concentration was varied from 2.0mM to 4.0mM by keeping the iron concentration constant as 0.05mM. At the H_2O_2 concentration of 2mM the 2-NA and COD removal obtained was 62.4 % and 45.2%, for 2.5mM of H_2O_2 concentration the removal efficiencies observed to be, 69.5% and 54.5 % respectively for 2-NA and COD removal. When the H_2O_2 concentration was increased to 3.0mM, the 2-NA and COD removal was increased to 77.4 % and 60.2%. Further increase in the H_2O_2 concentration to 3.5mM the maximum removal of 85.32 % of 2-NA and 69.9% of

COD removal was observed. H_2O_2 concentration was increased to 4.0mM the removal efficiencies were decreased to 80.4 % and 61.2 % for 2-NA and COD removal respectively. Figure 4.16 shows the removal efficiencies with respect to varying H_2O_2 concentration when the concentration of 2-NA was 0.5mM.

Figure 4.16: Effect of H_2O_2 concentration on removal of 2-Nitroaniline, (2-NA concentration: 0.5mM, Fe(LS) dosage: 0.05mM, pH = 2.5, Reaction Time =5hrs)

The experiments were further carried out for a higher concentration of 2-NA. The optimum H_2O_2 concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 2-NA concentration were 3.5mM, 7.5mM, 12mM, 16.5mM and 21mM respectively. Table 4.16 provides the maximum 2-NA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration at constant Fe(LS).

Table 4.16: Effect of H_2O_2 concentration on different initial concentration of 2-NA at constant Fe(LS) dosage

2-NA (mM)	Fe(LS) (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	2	62.4	45.2	40
		2.5	69.5	54.5	50
		3	77.4	60.2	60
		3.5	**85.3**	**69.9**	**70**

73

		4	80.4	61.2	80
1	0.1	4.0	65.1	51.5	40
		4.5	68.5	53.8	45
		5.0	71.1	54.1	50
		5.5	73.5	56.5	55
		6.0	76.5	57.1	60
		6.5	78.1	58.8	65
		7.0	80.5	61.5	70
		7.5	**82.5**	**66.4**	**75**
		8.0	80.4	63.1	80
1.5	0.15	8.0	57.5	44.2	53.3
		8.5	60.7	46.5	56.7
		9.0	62.2	48.2	60.0
		9.5	64.2	50.2	63.3
		10.0	70.5	52.4	66.7
		10.5	72.8	53.1	70.0
		11.0	76.2	55.2	73.3
		11.5	78.5	57.4	76.7
		12.0	**81.7**	**60.3**	**80.0**
		12.5	77.2	58.5	83.3
2.0	0.2	12.5	60.5	41.8	62.5
		13	63.2	43.2	65
		13.5	66.7	44.3	67.5
		14	70.4	45.4	70
		14.5	71.5	47.6	72.5
		15	73.9	48.7	75
		15.5	74.2	50.1	77.5
		16	76.3	55.1	80
		16.5	**78.5**	**58.2**	**82.5**
		17	75.7	55.4	85
2.5	0.25	17	55.1	40.6	68
		17.5	58.2	41.7	70

		18	60.3	43.8	72
		18.5	63.4	45.7	74
		19	65.4	46.5	76
		19.5	67.5	48.6	78
		20	70.6	50.2	80
		20.5	72.6	53.4	82
		21	**74.7**	**56.2**	**84**
		21.5	73.2	53.8	86

4.1.6.2 Effect Fe (LS) Concentration

After the optimization of H_2O_2 concentration, the iron dosage was optimized by varying the iron concentration from 0.025–0.1mM keeping the H_2O_2 concentration as constant as 3.5mM for 0.5mM of 2-NA concentration. When the iron concentration was 0.025mM, the removal efficiencies obtained was 79.4 % and 55.4 % for 2-NA and COD removal. The iron concentration was increased to 0.05mM the maximum removal efficiencies of 85.3% and 69.9% obtained for 2-NA and COD was observed. Further increase in iron concentration to 0.075mM the removal efficiencies decreased to 76.5% and 59.2% for 2-NA and COD respectively. For 0.1mM of iron concentration, the 2-NA and COD removal observed to be 70.7 % and 51.9% as shown in Figure 4.17. The Fe(LS) concentrations were optimized for higher concentrations of 2-NA. The optimum Fe(LS) concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 2-NA concentrations were 0.05, 0.1, 0.15, 0.2, 0.25mM respectively. Table 4.17 presents the results of 2-NA and COD removal efficiencies as a function of Fe(LS) concentration at a different initial concentration at constant H_2O_2.
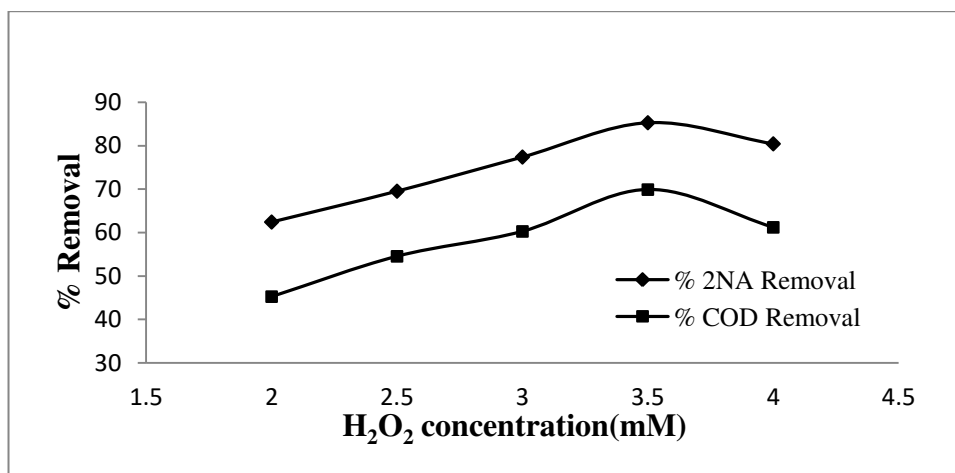
Figure 4.17: Effect of Fe(LS) concentration on removal of 2-Nitroaniline (2NA concentration: 0.5mM, H$_2$O$_2$ dosage: 3.5mM, pH = 2.5, Reaction Time =5hrs)

Table 4.17: Effect of Fe (LS) concentration on different initial concentration of 2-NA at constant H$_2$O$_2$ dosage

2-NA (mM)	H$_2$O$_2$ (mM)	Fe(LS) (mM)	% Removal	% COD removal	H/F ratio
0.5	3.5	0.025	79.4	55.4	140
		0.05	**85.3**	**69.9**	**70**
		0.075	76.5	59.2	46.7
		0.1	70.7	51.9	35
1	7.5	0.05	72.3	50.2	150
		0.075	78.7	55.8	100
		0.1	**82.5**	**66.4**	**75**
		0.125	78.8	59.5	60
1.5	12	0.1	71.4	48.5	120
		0.125	78.2	55.6	96
		0.15	**81.7**	**60.3**	**80**
		0.175	75.8	45.2	69
2.0	16.5	0.15	70.4	41.2	110
		0.175	75.9	49.6	94.2
		0.2	**78.5**	**58.2**	**82.5**
		0.225	75.2	51.4	73.3

		0.2	68.2	42.5	105
		0.225	71.5	45.3	93.3
2.5	21	**0.25**	**74.7**	**56.2**	**84**
		0.275	71.8	50.5	76.3

The experiments were conducted for the five different concentration viz. 0.5mM, 1.0mM, 1.5mM, 2.0mM and 2.5mM, using iron extracted from laterite soil as a catalyst. Table 4.18 summarizes the optimum H_2O_2 concentration and laterite iron concentration.

Table 4.18: Optimum dosages obtained during Fenton's oxidation of 2-Nitroaniline using Fe (LS) as a catalyst

Initial 2-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe (LS) (mM)	2-NA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	85.3	69.9	70
1.0	7.5	0.1	82.5	66.4	75
1.5	12.0	0.15	81.7	60.3	73.3
2.0	16.5	0.2	78.5	58.2	72.5
2.5	21	0.25	74.7	56.2	77.7

From the Table 4.3 and 4.18, it is observed that, the removal efficiencies obtained while using Fe(LS) as a catalyst were similar to those obtained while using FeSO$_4$, keeping the dosages of iron and H_2O_2 same in both the cases.

4.1.7 Fenton oxidation of 3-nitroaniline using laterite iron as a catalyst

4.1.7.1 Effect of H_2O_2 Concentration

The H_2O_2 concentration was varied from 2.5mM – 5.0mM for 3-NA concentration of 0.5mM. At 2.5mM of H_2O_2 concentration the 3-NA and COD removal obtained was 69.9% and 50.5% respectively. Further increase in H_2O_2

concentration to 3.0mM the removal efficiencies obtained was 71.5 % and 57.7% for 3-NA and COD removal respectively. At 3.5mM of H_2O_2 concentration, the 3-NA removal was 77.2% and COD removal was 61.8%. The 80.8% and 64.7% 3-NA and COD removal efficiency obtained at H_2O_2 concentration of 4.0mM. The maximum removal efficiencies obtained at H_2O_2 concentration of 4.5mM, 84.3% of 3-NA and 68.5% of COD removal was observed. When an H_2O_2 concentration increased to 5.0mM the removal efficiencies decreased to 79.4% and 65.5% for 3-NA and COD removal as shown in Figure 4.18. Hence the optimum H_2O_2 concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 3-NA concentration were 4.5mM, 9.5mM, 14.5mM, 19.5mM and 24.5mM respectively. Table 4.19 provides the 3-NA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration at constant Fe (LS).
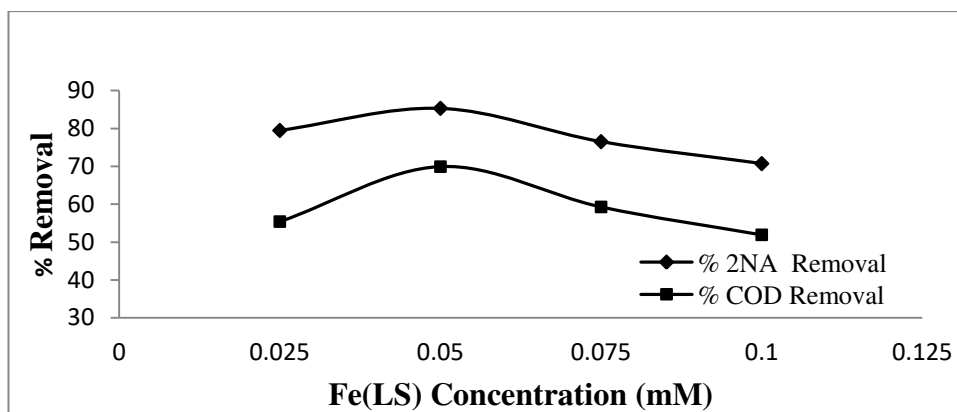

Figure 4.18: Effect of H_2O_2 concentration on removal of 3-Nitroaniline (3NA concentration: 0.5mM, Fe(LS) dosage: 0.05mM, pH: 2.5, Reaction Time: 5hrs)

Table: 4.19: Effect of H_2O_2 concentration on different initial concentration of 3-NA at constant Fe(LS) dosage

3-NA (mM)	Fe(LS) (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	2.5	69.9	50.59	50
		3	71.5	57.76	60

		3.5	77.2	61.89	70
		4	80.8	64.76	80
		4.5	**84.3**	**68.53**	**90**
		5.0	79.4	65.56	100
1.0	0.1	5.0	59.2	40.0	50
		5.5	62.4	42.7	55
		6.0	65.1	45.8	60
		6.5	68.5	48.9	65
		7.0	70.7	51.7	70
		7.5	72.1	53.6	75
		8.0	75.6	54.5	80
		8.5	78.4	56.4	85
		9.0	80.6	58.3	90
		9.5	**82.5**	**61.6**	**95**
		10	79.2	57.3	100
1.5	0.15	10	60.6	41.3	66.7
		10.5	63.2	43.2	70
		11	65.7	46.7	73.4
		11.5	67.5	48.8	76.7
		12	70.5	49.5	80
		12.5	72.8	50.1	83.4
		13	74.3	53.1	86.7
		13.5	77.5	55.3	90
		14	78.5	58.6	93.4
		14.5	**80.3**	**59.9**	**96.7**
		15	78.4	57.9	100
2.0	0.2	15.00	52.5	35.2	75
		15.5	55.3	37.5	77.5
		16	57.6	38.4	80
		16.5	60.7	40.5	82.5
		17	61.8	43.9	85
		17.5	65.6	45.4	87.5

		18	67.7	47.7	90
		18.5	70.5	50.4	92.5
		19	73.2	52.3	95
		19.5	**75.2**	**55.9**	**97.5**
		20	72.5	53.2	100
2.5	0.25	20	50.2	33.4	80
		20.5	55.6	35.5	82
		21	67.8	37.4	84
		21.5	60.7	40.7	86
		22	61.9	42.6	88
		22.5	63.2	45.8	90
		23	66.5	46.6	92
		23.5	68.8	48.71	94
		24	70.3	50.88	96
		24.5	**71.6**	**52.24**	**98**
		25	69.4	49.64	100

4.1.7.2 Effect Fe(LS) Concentration

The laterite iron concentration was optimized by varying the laterite iron concentration from 0.025-0.1mM by keeping the H_2O_2 concentration constant as 4.5mM for 0.5mM of 3-NA concentration. Initially, the laterite iron concentration was 0.025 mM; the 3-NA and COD removal obtained was 80.2% and 62.5% respectively. The laterite iron concentration was increased to 0.5mM; the removal efficiencies obtained was 84.3 % and 68.5% respectively for 3-NA and COD removal. The laterite iron concentration further increased to 0.075 and 0.1mM, the removal of 3-NA and COD obtained was 79.1% and 60.3% and 76.2% and 55.4% respectively as shown in Figure 4.19. The optimum Fe(LS) concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5mM of initial 3-NA concentrations were 0.05, 0.1, 0.15, 0.2, 0.25mM respectively. Table 4.20 presents the results of 3-NA and COD removal efficiencies as a function of Fe(LS) concentration at a different initial concentration at constant H_2O_2.
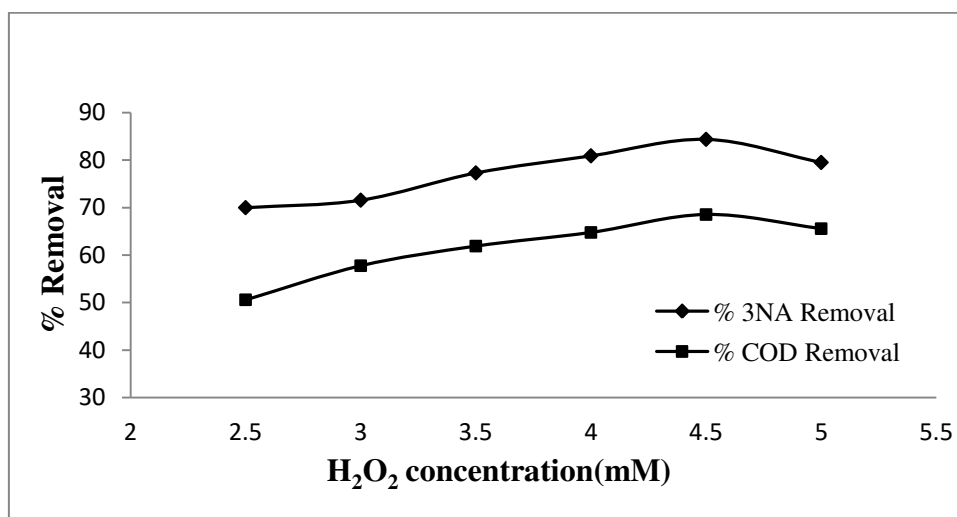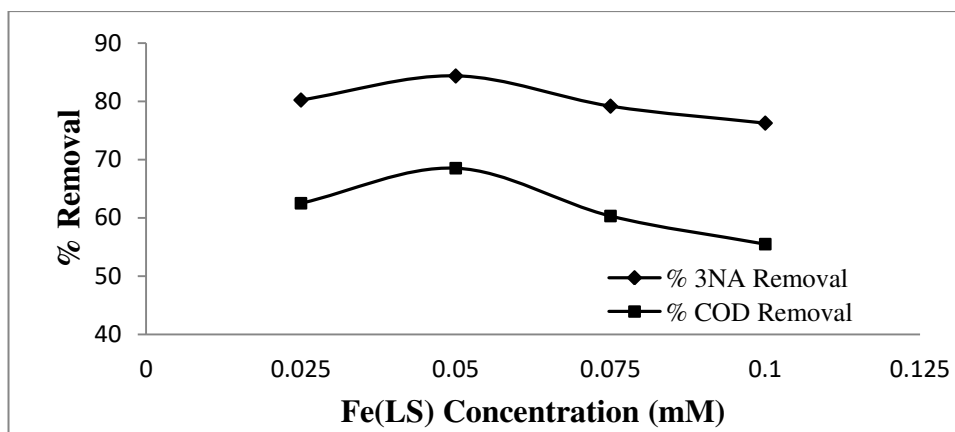
Figure 4.19: Effect of Fe(LS) concentration on removal of 3-Nitroaniline (3-NA concentration: 0.5mM, H$_2$O$_2$ dosage: 4.5mM, pH = 2.5, Reaction Time =5hrs)

Table 4.20: Effect of Fe (LS) concentration on different initial concentration of 3-NA at constant H$_2$O$_2$ dosage

3-NA (mM)	H$_2$O$_2$ (mM)	Fe (LS) (mM)	% Removal	% COD removal	H/F ratio
0.5	4.5	0.025	80.2	62.5	180
		0.05	**84.3**	**68.5**	**90**
		0.075	79.1	60.3	60
		0.1	76.2	55.4	45
1	9.5	0.05	73.8	55.1	190.0
		0.075	78.5	59.2	126.7
		0.1	**82.5**	**61.5**	**95.0**
		0.125	77.2	57.5	76.0
1.5	14.5	0.1	73.4	52.3	145.0
		0.125	77.7	56.7	116.0
		0.15	**80.3**	**59.9**	**96.7**
		0.175	78.9	57.2	82.9
2.0	19.5	0.15	68.2	49.8	130.0
		0.175	71.5	52.7	111.4
		0.2	75.2	55.9	97.5
		0.225	70.7	51.2	86.7

81

		0.2	65.2	45.9	122.5
2.5	24.5	0.225	68.7	51.8	108.9
		0.25	**71.6**	**52.2**	**98.0**
		0.275	67.9	49.3	89.1

The optimized dosages obtained for the higher concentration of 3-NA and summarized in Table 4.21.

Table 4.21: Optimum dosages of H_2O_2 and Fe obtained during Fenton's oxidation of 3-Nitroaniline using Fe (LS) as a catalyst

Initial 3-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe (LS) concentration (mM)	3-NA removal (%)	COD removal (%)	H/F ratio
0.5	4.5	0.05	84.3	68.5	90
1.0	9.5	0.1	82.5	61.5	95
1.5	14.5	0.15	80.3	59.1	96.6
2.0	19.5	0.2	75.2	55.9	97.5
2.5	24.5	0.25	71.6	52.2	98

From the Table 4.6 and 4.21, it is observed that, almost similar efficiencies observed after using Fe(LS) as a catalyst as compared to those obtained while using $FeSO_4$, keeping the dosages of iron and H_2O_2 same in both the cases.

4.1.8. Fenton oxidation of 4-Nitroaniline using laterite iron as a catalyst

4.1.8.1 Effect of H_2O_2 Concentration

The iron extracted from laterite soil was used as a source of iron as a catalyst for the Fenton's oxidation. The H_2O_2 concentration was optimized by varying the concentration from 4.0mM-5.5mM by keeping iron concentration constant as 0.05mM for 0.5mM of 4-NA concentration. The optimization started with the H_2O_2 concentration of 4.0mM, the 4-NA and COD removal observed to be 91.3% and

78.9%. Increase in the H_2O_2 concentration to 4.5mM the 4-NA and COD removal increased to 94.5% and 81.4% respectively. The maximum removal obtained at H_2O_2 concentration of 5.0mM i.e. 98.7% for 4-NA removal and 84.7% for COD removal. The increase in H_2O_2 concentration to 5.5mM, the 4-NA and COD removal decreased to 95.5% and 82.2% respectively as shown in the Figure. 4.20. The optimized hydrogen peroxide dosages for 0.5, 1, 1.5, 2, 2.5mM of 4-NA concentration were 5, 10.5, 16, 21.5 and 27mM respectively. Table 4.22 provides the 4-NA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration at constant Fe(LS).
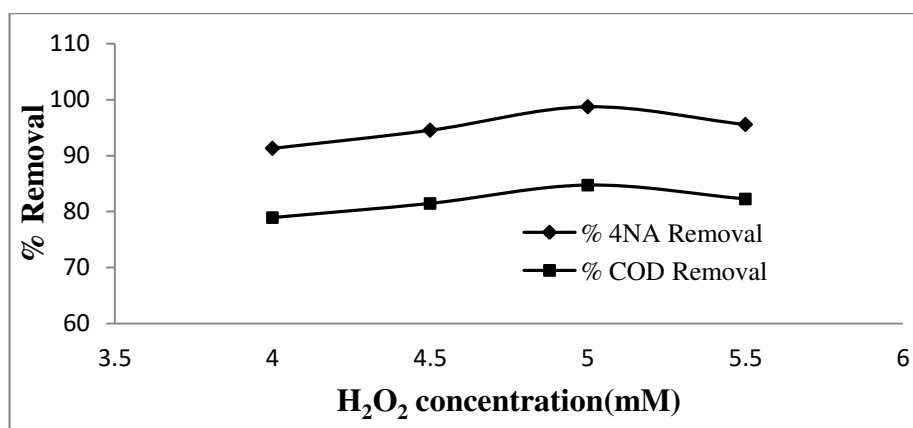
Figure 4.20: Effect of H_2O_2 concentration on removal of 4-Nitroaniline (4-NA concentration: 0.5mM, Fe(LS) dosage: 0.05mM, pH = 3.0, Reaction Time =5hrs)

Table 4.22: Effect of H_2O_2 concentration on different initial concentration of 4-NA at constant Fe(LS) dosage

4-NA (mM)	Fe(LS) (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	4	91.3	78.9	80
		4.5	94.5	81.4	90
		5	**98.7**	**84.7**	**100**
		5.5	95.5	82.2	110
1.0	0.1	5.5	81.2	65.1	55
		6.0	82.3	66.3	60

		6.5	84.5	68.5	65
		7.0	86.9	70.5	70
		7.5	87.2	71.4	75
		8.0	89.5	72.1	80
		8.5	91.1	73.5	85
		9.0	92.3	75.8	90
		9.5	93.6	77.4	95
		10.0	95.7	78.4	100
		10.5	**96.1**	**80.7**	**105**
		11.0	93.3	77.6	110
1.5	0.15	11.0	76.6	60.5	73
		11.5	78.2	61.5	77
		12.0	79.5	63.6	80
		12.5	81.2	66.5	83
		13.0	83.3	67.2	87
		13.5	85.5	69.3	90
		14.0	87.5	70.4	93
		14.5	88.1	71.8	97
		15.0	90.8	72.5	100
		15.5	92.8	73.5	103
		16.0	**94.7**	**76.5**	**107**
		16.5	91.5	73.6	110
2.0	0.2	16.5	74.3	58.8	83
		17.0	75.5	60.2	85
		17.5	76.6	61.1	88
		18.0	77.7	62.4	90
		18.5	80.8	63.5	93
		19.0	81.9	66.2	95
		19.5	84.7	69.3	98
		20.0	86.8	71.4	100
		20.5	88.7	72.5	103
		21.0	89.1	74.1	105

		21.5	91.5	75.3	108
		22.0	88.2	73.8	110
		22.0	72.5	60.5	88
		22.5	73.5	61.5	90
		23.0	75.9	63.6	92
		23.5	76.9	66.5	94
		24.0	77.5	67.2	96
2.5	0.25	24.5	80.3	69.3	98
		25.0	83.2	70.4	100
		25.5	85.2	71.8	102
		26.0	86.3	72.5	104
		26.5	88.3	73.5	106
		27.0	90.5	76.5	108
		27.5	87.4	73.6	110

4.1.8.2 Effect of Fe(LS) Concentration

The laterite iron concentration was optimized after the optimization of H_2O_2 concentration. For 0.5 mM of 4-NA concentration, Fe(LS) concentration was varied from 0.025 mM - 0.1 mM. When the iron concentration was 0.025mM, the 4-NA and COD removal observed was 93.3% and 80.6%. For 0.05mM of H_2O_2 concentration, 4-NA and COD removal observed were 98.7% and 84.7% respectively. The increase in the iron concentration to 0.075mM and 0.1mM, the 4-NA and COD removal were, 95.5% and 79.5% and 91.2% and 76.9% respectively as shown in Figure 4.21. The optimum Fe(LS) concentration obtained for 0.5, 1.0, 1.5, 2.0 and 2.5 mM of initial 4-NA concentrations were 0.05, 0.1, 0.15, 0.2 and 0.25 mM respectively. Table 4.23 provides the 4-NA and COD removal efficiencies as a function of laterite iron concentration.
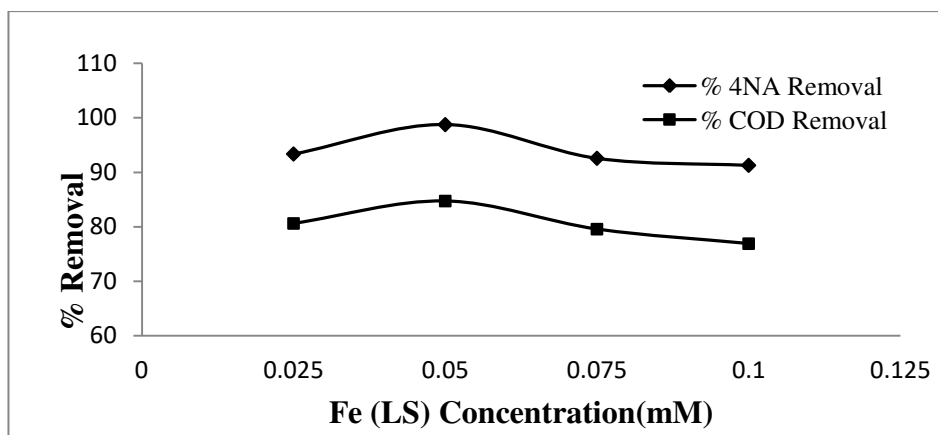
Figure 4.21: Effect of Fe(LS) concentration on removal of 4-Nitroaniline (4-NA concentration: 0.5mM, H₂O₂ dosage: 5.0mM, pH = 3.0, Reaction Time =5hrs)

Table 4.23: Effect of Fe(LS) concentration on different initial concentration of 4-NA at constant H₂O₂ dosage

4-NA (mM)	H₂O₂ (mM)	Fe(LS) (mM)	% Removal	% COD removal	H/F ratio
0.5	5	0.025	93.3	80.6	200
		0.05	**98.7**	**84.7**	**100**
		0.075	92.5	79.5	66.7
		0.1	91.2	76.9	50
1	10.5	0.05	89.3	78.7	210.0
		0.075	92.5	78.5	140.0
		0.1	**96.1**	**80.7**	**105**
		0.125	93.9	78.6	84.0
1.5	16	0.1	90.1	70.2	160.0
		0.125	92.3	73.0	128.0
		0.15	**94.7**	**76.5**	**106.7**
		0.175	91.4	72.1	91.4
2.0	21.5	0.15	86.4	70.5	143.3
		0.175	88.1	72.4	122.9
		0.2	**91.5**	**75.3**	**107.5**
		0.225	87.8	71.2	95.6

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		0.2	83.5	67.2	135.0
2.5	27	0.225	85.7	70.8	120.0
		0.25	**90.5**	**76.5**	**108.0**
		0.275	86.3	68.5	98.2

Then for the higher concentration of 4NA viz.1.0mM, 1.5mM, 2.0mM and 2.5mM, the optimization studies were carried out in a similar way as explained for 0.5mM. The optimized for dosages of H_2O_2 concentration and laterite iron concentration are as shown in Table 4.24.

Table 4.24: Optimum dosages obtained during Fenton's oxidation of 4-Nitroaniline using Fe (LS) as a catalyst

Initial 4-NA concentration (mM)	H_2O_2 con mM)	Fe(LS) con (mM)	4-NA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	98.7	84.7	100
1.0	10.5	0.1	96.1	80.7	105
1.5	16.0	0.15	94.7	76.5	106.6
2.0	21.5	0.2	91.5	75.3	107.5
2.5	27.0	0.25	90.5	72.8	108

After comparing the Table 4.9 and 4.24, it is observed that the removal efficiencies observed were almost similar while using the Fe(LS) concentration as compare to $FeSO_4$. The optimum hydrogen peroxide and iron dosages obtained for the maximum removal efficiencies were similar.

4.1.9. Fenton oxidation of 2-Methoxyaniline using laterite iron as a catalyst

4.1.9.1 Effect of H_2O_2 Concentration

The effect of H_2O_2 concentration in Fenton's oxidation was studied for different concentration of 2-MA viz: 0.5-2.5mM at an interval of 0.5mM. Initially, the

studies were carried out for 0.5mM of 2-MA concentration. The H_2O_2 concentration was varied from 2.5mM to 4.5mM as shown in Figure 4.22. When the H_2O_2 concentration was 2.5mM the 2-MA and COD removal obtained was 66.7% and 55.5%, then the H_2O_2 concentration was increased to 3.0mM, the removal efficiencies obtained were 70.6% and 60.7% respectively for 2-MA and COD removal. The increase in H_2O_2 concentration to 3.5mM, the maximum removal efficiencies obtained were 76.9% and 65.2% respectively for 2-MA and COD removal. The increase in H_2O_2 concentration to 4.0mM, the removal efficiency decreased to 72.4% and 61.5% for 2-MA and COD removal. Further increase in the H_2O_2 concentration to 4.5mM, the 2-MA and COD removal efficiencies obtained were 67.5% and 54.9% respectively. The optimum hydrogen peroxide dosages obtained for 0.5 1, 1.5, 2 and 2.5mM 2-MA concentrations were 3.5, 7.5 11.5, 15.5 and 19.5mM respectively. The Table 4.25 provides the 2-MA removal and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration at constant Fe (LS).
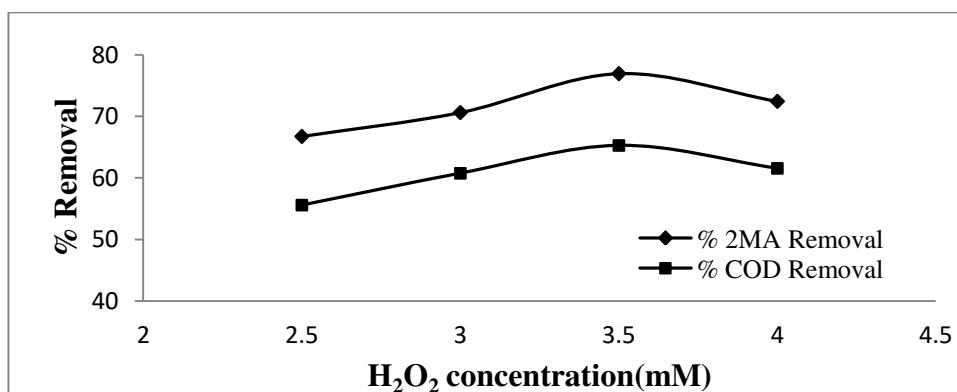

Figure 4.22: Effect of H_2O_2 concentration on removal of 2-Methoxyaniline (2MA concentration: 0.5mM, Fe(LS) dosage: 0.05mM, pH = 3.0, Reaction Time =5hrs)

Table 4.25: Effect of H_2O_2 concentration on different initial concentration of 2-MA at constant Fe(LS) dosage

2-MA (mM)	Fe(LS) (mM)	H_2O_2 (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	2.5	66.7	55.5	50

		3	70.6	60.7	60
		3.5	**76.9**	**65.2**	**70**
		4	72.4	61.5	80
		4.5	67.5	54.9	90
1.0	0.1	4.5	65.3	53.6	45
		5	67.8	54.6	50
		5.5	68.1	55.8	55
		6	70.6	57.7	60
		6.5	71.3	58.3	65
		7	73.4	60.2	70
		7.5	**75.4**	**62.5**	**75**
		8	74.4	59.2	80
1.5	0.15	8	60.5	45.8	53.4
		8.5	62.2	47.2	56.7
		9	63.7	49.9	60
		9.5	65.5	50.5	63.3
		10	66.6	52.1	66.6
		10.5	67.7	54.7	70
		11	69.9	56.5	73.3
		11.5	**71.7**	**58.3**	**76.6**
		12	70.2	55.1	80
2.0	0.2	12	57.2	43.2	60
		12.5	60.5	45.8	62.5
		13	62.2	47.2	65
		13.5	63.7	49.9	67.5
		14	65.5	50.5	70
		14.5	66.6	52.1	72.5
		15	67.7	54.7	75
		15.5	**69.2**	**55.4**	**77.5**
		16	66.2	51.6	80
2.5	0.25	16	53.2	42.7	64
		16.5	55.7	43.5	66

		17	57.2	44.1	68
		17.5	58.5	45.1	70
		18	60.7	46.5	72
		18.5	61.1	48.6	74
		19	62.2	49.7	76
		19.5	**63.4**	**53.2**	**78**
		20	61.8	48.7	80

4.1.9.2 Effect of Fe(LS) Concentration

The laterite iron concentration was optimized after the optimization of H_2O_2 concentration. The laterite iron concentration varied from 0.025mM to 0.1mM for 0.5mM of 2-MA concentration. The removal efficiencies obtained at 0.025mM of laterite iron concentration was 71.6% of 2-MA and 60.2% of COD removal. The maximum removal of 76.9% and 65.2% of 2-MA and COD removal were obtained at 0.05mM of Fe(LS) dosage. Further increase in laterite iron concentration to 0.075mM and 0.1mM, the removal efficiencies decreased i.e. 72.5% and 61.3% for 2-MA and COD removal and 64.12% and 55.1% respectively as shown in Figure 4.23. Similar studies were also carried out for a higher concentration of 2-MA. Hence the optimized Fe(LS) concentration for 0.5, 1, 1.5, 2 and 2.5mM of 2-MA concentrations were 0.05, 0.1, 0.15, 0.2 and 0.25mM. Table 4.26 presents the results of 2-MA and COD removal efficiencies as a function of Fe(LS) concentration at a different initial concentration at constant H_2O_2.
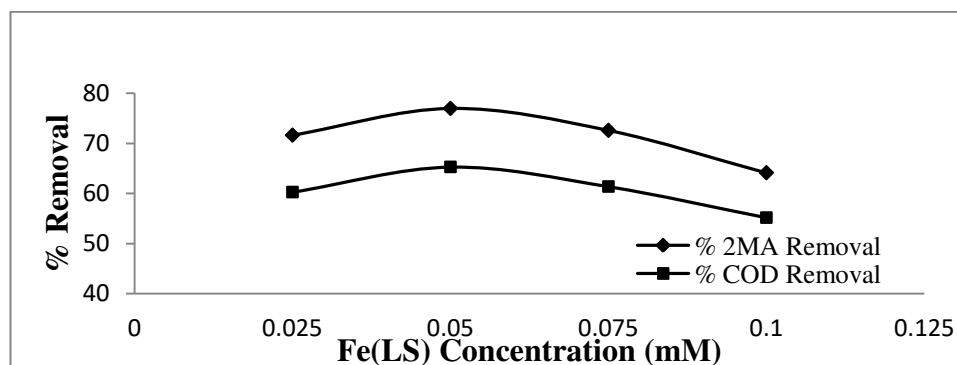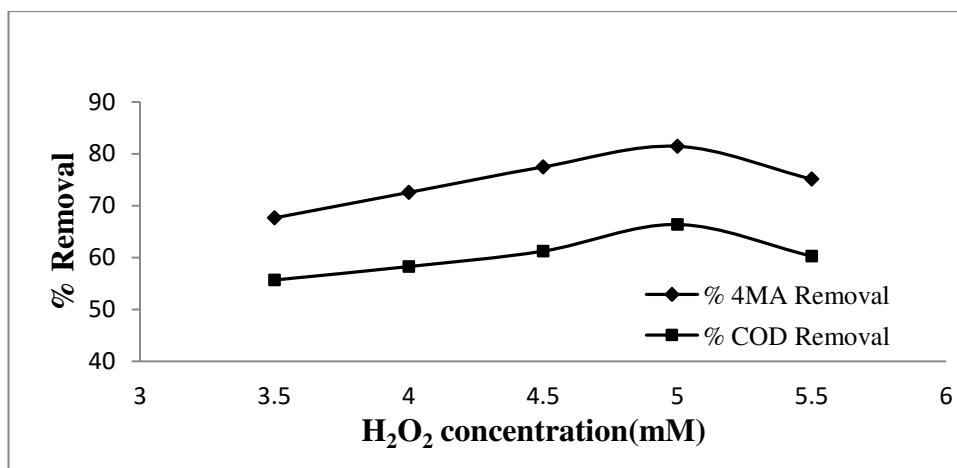

Figure 4.23: Effect of Fe(LS) concentration on removal of 2-Methoxyaniline (2-MA concentration: 0.5mM, H_2O_2 dosage: 3.5mM, pH = 3.0, Reaction Time=5hrs)

Table 4.26: Effect of Fe(LS) concentration on different initial concentration of 2-MA at constant H_2O_2 dosage

2-MA (mM)	H_2O_2 (mM)	Fe(LS) (mM)	% Removal	% COD removal	H/F ratio
0.5	3.5	0.025	71.6	60.2	140
		0.05	**76.9**	**65.2**	**70**
		0.075	72.5	61.3	46.7
		0.1	64.1	55.1	35
1	7.5	0.05	66.7	55.4	150
		0.075	70.7	57.7	100
		0.1	**75.4**	**62.5**	**75**
		0.125	73.5	60.3	60
1.5	11.5	0.1	64.5	47.2	115
		0.125	67.8	50.1	92
		0.15	**71.7**	**58.3**	**76.7**
		0.175	68.56	56.3	65.7
2.0	15.5	0.15	61.5	47.9	103.4
		0.175	66.2	51.8	88.5
		0.2	**69.2**	**55.4**	**77.5**
		0.225	65.5	50.3	68.9
2.5	19.5	0.2	55.6	40.5	97.5
		0.225	59.6	42.7	86.7
		0.25	**63.4**	**53.2**	**78**
		0.275	60.2	49.7	70.9

Similarly, optimization studies were conducted for a higher concentration of 2-MA concentration. The removal efficiencies obtained for the higher concentration of 2-MA and optimum H_2O_2 concentration and Fe(LS) concentration are as shown in Table 4.27.

After comparing the Table 4.12 and 4.27, it is observed that, the removal efficiencies obtained during the Fenton's oxidation using $FeSO_4$ and Fe(LS) as a catalyst were almost similar. It indicated that Fe(LS) could also achieve similar

removal efficiencies for the same hydrogen peroxide and iron dosages.

Table 4.27: Optimum dosages obtained during Fenton's oxidation of 2-Methoxyaniline using Fe (LS) as a catalyst

Initial 2-MA Concentration (mM)	H_2O_2 Concentration (mM)	Fe(LS) concentration (mM)	2-MA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	76.9	65.2	70
1.0	7.5	0.1	75.4	62.5	75
1.5	11.5	0.15	71.7	58.3	76.6
2.0	15.5	0.2	69.2	55.4	77.5
2.5	19.5	0.25	63.4	53.2	78

4.1.10 Fenton oxidation of 4-Methoxyaniline using laterite iron as a catalyst

4.1.10.1 Effect of H_2O_2 Concentration

The Fenton's oxidation of 4-Methoxyaniline was carried out using iron extracted from laterite soil as a catalyst. The experiments were carried out by varying H_2O_2 and iron concentration. Initially, the H_2O_2 concentration was varied from 3.5mM to 5.5mM by keeping the iron concentration constant as 0.05mM for 0.5mM of 4-MA concentration is as shown in Figure 4.24. At the H_2O_2 concentration of 3.5mM the 4-MA and COD removal obtained was 67.6 % and 55.7%, for 4.0mM of H_2O_2 concentration the removal efficiencies observed to be, 72.5% and 58.2 % respectively for 4-MA and COD. When the H_2O_2 concentration was increase to 4.5mM, the 4-MA and COD removal was increased to 77.4 % and 61.2%. At the H_2O_2 concentration of 5.0mM, the maximum removal efficiencies of 81.4% of 4-MA and 66.4% of COD removal were observed. Further increase in the H_2O_2 concentration to 5.5mM the removal efficiencies were decreased to 78.1 % and 60.3 % for 4-MA and COD removal respectively. The optimized H_2O_2 dosages obtained for 0.5, 1, 1.5,2, 2.5mM of 4-MA concentration were 5, 10.5, 16, 21.5 and 27mM. Table 4.28 provides the 4-MA and COD removal efficiencies as a function of initial concentration at different H_2O_2 concentration at constant Fe (LS).
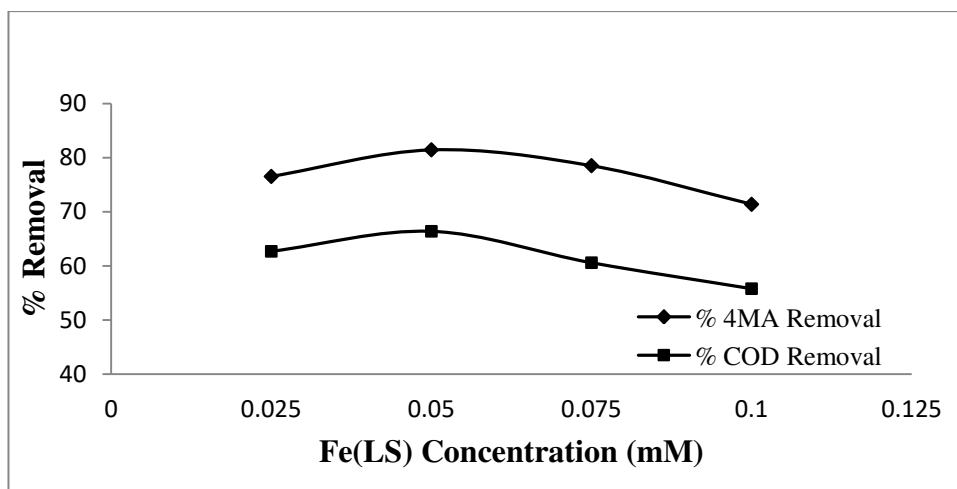
Figure 4.24: Effect of H$_2$O$_2$ concentration on removal of 4-Methoxyaniline (4-MA concentration: 0.5mM, Fe(LS) dosage: 0.05mM, pH = 3.0, Reaction Time =5hrs)

Table 4.28: Effect of H$_2$O$_2$ concentration on different initial concentration of 4-MA at constant Fe(LS) dosage

4-MA (mM)	Fe(LS) (mM)	H$_2$O$_2$ (mM)	% Removal	% COD removal	H/F ratio
0.5	0.05	3.5	67.6	55.7	70
		4.0	72.5	58.2	80
		4.5	77.4	61.2	90
		5	**81.4**	**66.4**	**100**
		5.5	78.1	60.3	110
1.0	0.1	5.5	57.7	35.2	55
		6	60.3	39.4	60
		6.5	63.1	42.2	65
		7	65.4	45.6	70
		7.5	67.7	47.5	75
		8.0	69.4	50.5	80
		8.5	72.3	52.2	85
		9	74.3	54.3	90
		9.5	77.5	58.3	95
		10	79.2	61.5	100

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		10.5	80.6	63.8	105
		11	78.6	61.2	110
1.5	0.15	11	53.6	36.9	73.3
		11.5	55.9	40.6	76.6
		12	57.7	42.5	80
		12.5	60.3	45.8	83.3
		13	61.4	48.1	86.6
		13.5	63.3	50.8	90
		14	67.7	53.2	93.3
		14.5	69.4	55.3	96.6
		15	72.2	56.5	100
		15.5	73.2	58.6	103.3
		16	**78.1**	**61.2**	**106.6**
		16.5	75.4	57.8	110
2.0	0.2	16.5	52.5	33.6	82.5
		17	55.7	35.7	85
		17.5	58.4	37.6	87.5
		18	60.4	40.5	90
		18.5	62.5	42.6	92.5
		19	65.4	44.6	95
		19.5	66.8	46.9	97.5
		20	68.4	49.7	100
		20.5	70.2	52.7	102.5
		21	71.2	54.3	105
		21.5	**72.3**	**56.3**	**107.5**
		22	70.3	51.5	110
2.5	0.25	22	43.7	30.5	88
		22.5	45.3	32.6	90
		23	48.6	35.8	92
		23.5	51.9	37.8	94
		24	53.6	40.6	96
		24.5	55.8	42.4	98

		25	57.7	45.6	100
		25.5	60.3	48.8	102
		26	61.4	50.8	104
		26.5	64.7	52.6	106
		27	**67.6**	**55.2**	**108**
		27.5	65.4	51.2	110

4.1.10.2 Effect of Fe(LS) concentration

The iron dosage was optimized by varying the iron concentration from 0.025–0.1mM keeping the H_2O_2 concentration as constant as 5.0mM. When the iron concentration was 0.025mM, the removal efficiencies obtained were 76.5 % and 62.7 % for 4-MA and COD respectively. When the iron concentration was increased to 0.05mM the maximum removal efficiencies of 81.4% and 66.4% for 4-MA and COD were observed respectively. Further increase in iron concentration to 0.075mM the removal efficiencies decreased to 78.5% and 60.6% for 4-MA and COD respectively. For 0.1mM of iron concentration, the 4-MA and COD removal were observed to be 71.3 % and 55.8% respectively, as shown in Figure 4.25. The experiments were further carried out for higher concentrations of 4-MA and the optimum Fe(LS) concentrations obtained for 0.5, 1, 1.5, 2 and 2.5mM of 4-MA were 0.05, 0.1, 0.15, 0.2 and 0.25mM . Table 4.29 presents the results of 4-MA and COD removal efficiencies as a function of Fe(LS) concentration at a different initial concentration at constant H_2O_2.

Figure 4.25: Effect of Fe(LS) concentration on removal of 4-Methoxyaniline (4-MA concentration: 0.5mM, H$_2$O$_2$ dosage: 5.0mM, pH = 3.0, Reaction Time =5hrs)

Table 4.29: Effect of Fe(LS) concentration on different initial concentration of 4-MA at constant H$_2$O$_2$ dosage

4-MA (mM)	H$_2$O$_2$ (mM)	Fe(LS) (mM)	% Removal	% COD removal	H/F ratio
0.5	5	0.025	76.5	62.7	200
		0.05	**81.4**	**66.4**	**100**
		0.075	78.5	60.6	66.7
		0.1	71.3	55.8	50
1	10.5	0.05	70.5	54.2	210
		0.075	75.3	60.1	140
		0.1	**80.6**	**63.8**	**105**
		0.125	74.5	58.4	84
1.5	16	0.1	69.7	50.5	160
		0.125	74.5	57.6	128
		0.15	**78.1**	**61.2**	**106.7**
		0.175	75.6	57.7	91.4
2.0	21.5	0.15	63.6	48.2	143.4
		0.175	67.7	51.8	122.8
		0.2	**72.3**	**56.3**	**107.5**

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		0.225	69.8	50.6	95.5
		0.2	60.3	47.5	135
		0.225	63.6	51.7	120
2.5	27	**0.25**	**67.6**	**55.2**	**108**
		0.275	64.3	52.6	98.1

The experiments were conducted for five different concentration viz. 0.5mM, 1.0mM, 1.5mM, 2.0mM and 2.5mM using iron extracted from laterite soil as a catalyst. Table 4.30 summarizes the optimum H_2O_2 concentration and laterite iron concentration for different concentration of 4-MA.

After comparing the results presented in Table 4.15 and 4.30, it is observed that the removal efficiencies observed were almost similar while using the Fe(LS) concentration as compared to $FeSO_4$. The optimum hydrogen peroxide and iron dosages obtained for the maximum removal efficiencies were similar.

Table 4.30: Optimum dosages obtained during Fenton's oxidation of 4-Methoxyaniline using Fe (LS) as a catalyst

Initial 4-MA Concentration (mM)	H_2O_2 Concentration (mM)	Fe(LS) concentration (mM)	4-MA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	81.4	66.4	100
1.0	10.5	0.1	80.6	63.8	105
1.5	16.0	0.15	78.1	61.2	106.6
2.0	21.5	0.2	72.3	56.3	107.5
2.5	27.0	0.25	67.6	55.2	108

From the present study, it has been observed that the locally available laterite can also be used as a source of iron which will generate enough hydroxyl radicals. The removal efficiencies obtained during the conventional Fenton's oxidation process is comparable with the results obtained with the Fe(LS). The almost similar removal efficiencies obtained with the same optimum dosages as that of conventional methods,

indicated the replacement of conventional ferrous salt by Fe(LS) so that the cost of the operations becomes less hence its economical.

4.2 PHOTO FENTON OXIDATION OF ANILINE DERIVATIVES

It has been reported in the literature that (Fonseca et al., 2010), Photo Fenton oxidation process enhances the oxidation by generating the OH radials faster which improves the removal efficiencies. The photo-Fenton experiments were carried out using $FeSO_4$ and iron extracted from locally available laterite soil as an alternative catalyst. The experiments were carried out at optimized pH, hydrogen peroxide and iron obtained during the Fenton's process and for the reaction time of 2 hrs. The experimental results are presented below.

4.2.1 Photo - Fenton oxidation of 2-Nitroaniline using $FeSO_4$ as iron catalyst

The photo-Fenton oxidation was carried out for the optimized dosages of the 2-NA. For 0.5mM of 2-NA concentration, the 2-NA removal efficiency increased from 89.1% to 93.8 % and COD removal efficiency increased from 73 % to 78.3%. Then for 1mM of 2-NA concentration, 2-NA and COD removal increased from 88.3 % and 69.1% to 91.9 % and 73.9 % respectively. Further, the studies continued for 1.5mM concentration, the 2-NA and COD removal obtained were 90.8% and 68.8% respectively whereas the in Fenton's oxidation, the 2-NA and COD removal obtained were 86.4% and 65.4%. Then for the 2mM of 2-NA, the 2-NA and COD removal efficiency increased from 81.4 % and 61.6% to 85.6% and 64.5% respectively. For 2.5mM of 2-NA concentration, the 2-NA removal efficiency increased from 78% to 81.8 % and COD removal efficiency increased from 58.2% to 60.6%. The Table 4.31 summarizes the removal efficiencies obtained for the different initial concentration of 2-NA. It was found that removal efficiency was maximum when the initial concentration of 2-NA was 0.5mM. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

Table 4.31: Removal efficiencies obtained during photo-Fenton oxidation of 2-Nitroaniline using FeSO₄ as iron catalyst

Initial 2-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} concentration (mM)	2-NA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	93.8	78.3	70
1.0	7.5	0.1	91.9	73.9	75
1.5	11.0	0.15	90.8	68.8	80
2.0	14.5	0.2	85.6	64.5	82.5
2.5	17.5	0.25	81.8	60.6	84

4.2.2 Photo Fenton oxidation of 3-Nitroaniline using FeSO₄ as iron catalyst

The photo-Fenton oxidation of 3-NA was carried out at optimum dosages obtained during the Fenton's oxidation process. The 3-NA and COD removal efficiency obtained during the photo-Fenton oxidation process are tabulated in Table 4.32.

Table 4.32: Removal efficiencies obtained during photo-Fenton's oxidation of 3-Nitroaniline using FeSO₄ as iron catalyst

Initial 3-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe^{2+} concentration (mM)	3-NA removal (%)	COD removal (%)	H/F ratio
0.5	4.5	0.05	90.7	75.8	90
1.0	9.5	0.1	89.8	69.5	95
1.5	14.5	0.15	87.9	66.8	96.6
2.0	19.5	0.2	82.2	62.9	97.5
2.5	24.5	0.25	79.4	59.7	98

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 3-NA concentration, the removal efficiency of 3-NA increased from

88.7% in Fenton to 90.7% in photo-Fenton and the COD removal increased from 71.7% in Fenton to 75.8% in photo-Fenton. Similar trends were observed for a higher concentration of 3-NA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.3 Photo Fenton oxidation of 4-Nitroaniline using FeSO$_4$ as iron catalyst

The photo Fenton oxidation was carried out at the optimum doses obtained during Fenton's oxidation and results are tabulated in table 4.33 for the all the initial concentration of 4-NA. The maximum removal efficiencies obtained for a lower concentration of the 4-NA i.e. is 0.5mM concentration.

Table 4.33: Removal efficiencies obtained during photo-Fenton oxidation of 4-Nitroaniline using FeSO$_4$ as iron catalyst

Initial 4-NA Concentration (mM)	H$_2$O$_2$ Concentration (mM)	Fe^{2+} concentration (mM)	4-NA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	99.9	89.5	100
1.0	10.5	0.1	98.9	87.6	105
1.5	16.0	0.15	97.8	85.7	106.6
2.0	21.5	0.2	96.1	83.7	107.5
2.5	27.0	0.25	95.8	82.5	108

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 4-NA concentration, the removal efficiency of 4-NA increased from 99.8% in Fenton to 99.9% in photo-Fenton and the COD removal increased from 86.2% in Fenton to 89.5% in photo-Fenton. Similar trends were observed for a higher concentration of 4-NA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.4 Photo Fenton oxidation of 2-Methoxyaniline using FeSO$_4$ as iron catalyst

Table 4.34 shows the results obtained during the photo-Fenton oxidation of 2-MA at optimum conditions. The maximum removal efficiencies obtained were 86.2% and 74.1% for 2-MA and COD respectively for 0.5mM of 2-MA concentration.

Table 4.34: Removal efficiencies obtained during photo-Fenton oxidation of 2-Methoxyaniline using FeSO$_4$ as iron catalyst

Initial 2-MA Concentration (mM)	H$_2$O$_2$ Concentration (mM)	Fe^{2+} concentration (mM)	2-MA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	86.2	74.1	70
1.0	7.5	0.1	81.3	69.8	75
1.5	11.5	0.15	78.9	64.7	76.6
2.0	15.5	0.2	75.8	62.3	77.5
2.5	19.5	0.25	72.2	58.1	78

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 2-MA concentration, the removal efficiency of 2-MA increased from 82.4% in Fenton to 86.2% in photo-Fenton and the COD removal increased from 69.7% in Fenton to 74.1% in photo-Fenton. Similar trends were observed for a higher concentration of 2-MA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.5 Photo Fenton oxidation of 4-Methoxyaniline using FeSO$_4$ as iron catalyst

The photo-Fenton studies were further carried out for 4-MA at optimum dosages obtained during the Fenton's oxidation. Table 4.35 shows the removal efficiencies obtained during photo-Fenton oxidation of 4-MA at varying initial concentration.

Table 4.35: Removal efficiencies obtained during photo-Fenton oxidation of 4-Methoxyaniline using FeSO₄ as iron catalyst

Initial 4-MA Concentration (mM)	H₂O₂ Concentration (mM)	Fe²⁺ concentration (mM)	4-MA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	90.6	76.8	100
1.0	10.5	0.1	87.5	72.3	105
1.5	16.0	0.15	84.3	70.5	106.6
2.0	21.5	0.2	80.5	64.7	107.5
2.5	27.0	0.25	76.5	62.3	108

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 4-MA concentration, the removal efficiency of 4-MA increased from 85.5% in Fenton to 90.6% in photo-Fenton and the COD removal increased from 71.1% in Fenton to 76.8% in photo-Fenton. Similar trends were observed for a higher concentration of 4-MA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.6 Photo - Fenton oxidation of 2-Nitroaniline using laterite iron as a catalyst

The photo-Fenton's oxidation of 2-Nitroaniline was carried using iron extracted from laterite soil as a source of iron. The experiments were carried out at optimized dosages obtained during Fenton's oxidation of 2-NA. The Table 4.36 summarizes the removal efficiencies obtained for the different initial concentration of 2-NA.

Table 4.36: Removal efficiencies obtained during photo-Fenton oxidation of 2-Nitroaniline using Fe (LS) as a catalyst

Initial 2-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe (LS) concentration (mM)	2-NA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	90.7	74.9	70
1.0	7.5	0.1	87.6	70.5	75
1.5	12.0	0.15	85.5	63.9	80
2.0	16.5	0.2	82.9	61.5	82.5
2.5	21	0.25	78.8	59.9	84

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 2-NA concentration, the removal efficiency of 2-NA increased from 85.3% in Fenton to 90.7% in photo-Fenton and the COD removal increased from 69.9% in Fenton to 74.9% in photo-Fenton. Similar trends were observed for a higher concentration of 2-NA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.7 Photo - Fenton oxidation of 3-Nitroaniline using laterite iron as catalyst

The photo-Fenton oxidation of 3-NA is carried out at optimum dosages obtained during the Fenton's oxidation process using iron extracted from laterite soil as a source of iron. The 3-NA and COD removal efficiency obtained during the photo-Fenton oxidation process are tabulated in Table 4.37.

Table 4.37: Removal efficiencies obtained during photo-Fenton oxidation of 3-Nitroaniline using Fe (LS) as a catalyst

Initial 3-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe(LS) concentration (mM)	3-NA removal (%)	COD removal (%)	H/F ratio
0.5	4.5	0.05	88.7	73.6	90

1.0	9.5	0.1	86.5	65.7	95
1.5	14.5	0.15	84.7	63.8	96.6
2.0	19.5	0.2	79.8	58.7	97.5
2.5	24.5	0.25	75.8	55.7	98

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 3-NA concentration, the removal efficiency of 3-NA increased from 84.3% in Fenton to 88.7% in photo-Fenton and the COD removal increased from 68.5% in Fenton to 73.6% in photo-Fenton. Similar trends were observed for a higher concentration of 3-NA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.8 Photo - Fenton oxidation of 4-Nitroaniline using laterite iron as a catalyst

The photo-Fenton oxidation was carried out using iron extracted from laterite soil as a source of iron at the optimum doses obtained during Fenton's oxidation and results are tabulated in Table 4.38 for the all the initial concentration of 4-NA. The maximum removal efficiencies obtained for a lower concentration of the 4-NA i.e. is 0.5mM concentration.

Table 4.38: Removal efficiencies obtained during photo-Fenton oxidation of 4-Nitroaniline using Fe (LS) as a catalyst

Initial 4-NA Concentration (mM)	H_2O_2 Concentration (mM)	Fe (LS) concentration (mM)	4-NA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	99.1	87.9	100
1.0	10.5	0.1	97.8	84.8	105
1.5	16.0	0.15	96.8	80.8	106.6
2.0	21.5	0.2	93.3	78.4	107.5
2.5	27.0	0.25	92.6	73.2	108

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton oxidation. For 0.5mM of 4-NA concentration, the removal efficiency of 4-NA increased from 98.7% in Fenton to 99.1% in photo-Fenton and the COD removal increased from 84.7% in Fenton to 87.9% in photo-Fenton. Similar trends were observed for a higher concentration of 4-NA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.9 Photo-Fenton oxidation of 2-Methoxyaniline using laterite iron as a catalyst

The Table 4.39 show the results obtained during the photo-Fenton oxidation 2-MA using iron extracted from laterite soil as a source of iron at optimum conditions. The maximum removal efficiency obtained was 80.5% and 68.7% for 2-MA and COD removal respectively for 0.5mM of 2-MA concentration.

Table 4.39: Removal Efficiencies obtained during photo-Fenton oxidation of 2-Methoxyaniline using Fe (LS) as a catalyst

Initial 2-MA Concentration (mM)	H_2O_2 Concentration (mM)	Fe (LS) concentration (mM)	2-MA removal (%)	COD removal (%)	H/F ratio
0.5	3.5	0.05	80.5	68.7	70
1.0	7.5	0.1	78.7	66.8	75
1.5	11.5	0.15	75.8	63.5	76.6
2.0	15.5	0.2	72.3	58.4	77.5
2.5	19.5	0.25	67.5	56.6	78

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton's oxidation. For 0.5mM of 2-MA concentration, the removal efficiency of 2-MA increased from 76.9% in Fenton to 80.5% in photo-Fenton and the COD removal increased from 65.2% in Fenton to 68.7% in photo-Fenton. Similar trends were observed for a higher

concentration of 2-MA. It was observed that the overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation.

4.2.10 Photo-Fenton oxidation of 4-Methoxyaniline using laterite iron as a catalyst

The photo Fenton oxidation was carried out using iron extracted from laterite soil as a source of iron at the optimum doses obtained during Fenton's oxidation and results are tabulated in Table 4.40 for the all the initial concentration of 4-MA. The maximum removal efficiencies obtained for a lower concentration of the 4-MA i.e. is 0.5mM concentration.

Table 4.40: Removal efficiencies obtained during photo-Fenton oxidation of 4-Methoxyaniline using Fe (LS) as a catalyst

Initial 4-MA Concentration (mM)	H_2O_2 Concentration (mM)	Fe (LS) concentration (mM)	4-MA removal (%)	COD removal (%)	H/F ratio
0.5	5	0.05	85.5	70.3	100
1.0	10.5	0.1	83.8	66.7	105
1.5	16.0	0.15	81.5	64.8	106.6
2.0	21.5	0.2	76.7	60.6	107.5
2.5	27.0	0.25	71.3	59.5	108

It was observed from the previous set of results of Fenton's oxidation that, there was slight increase in the removal efficiencies during photo-Fenton's oxidation. For 0.5mM of 4-MA concentration, the removal efficiency of 4-MA increased from 81.4% in Fenton to 85.5% in photo-Fenton and the COD removal increased from 66.4% in Fenton to 70.3% in photo-Fenton. Similar trends were observed for a higher concentration of 4-MA.

It was observed that, for the selected aniline derivatives overall removal efficiency obtained during photo-Fenton oxidation was higher than Fenton's oxidation. Also the time required for the degradation during photo-Fenton was lesser than that required for Fenton's oxidation. This may be due to the fact that, the

regeneration of Fe^{2+} ions is more during photo-Fenton oxidation and which increases the production of OH radical, which increases the removal efficiency (Manu and Mahamood, 2011) .

4.3 KINETIC STUDIES OF THE ANILINE DERIVATIVES

In the present study, degradation of aniline derivatives by Fenton's and photo-Fenton process was studied using pseudo-first order reaction kinetics. The kinetic studies were conducted using the optimum dosages obtained during the degradation of the individual aniline derivatives by Fenton's oxidation process.

It is observed that the reaction rate is highest in the initial 30 minutes and hence the reaction kinetics was studied for a reaction time of 30 minutes. The expression for the kinetic model was as presented below (Kong and Lemley, 2006):

$$C_t / C_o = Kt + 1$$

where,

C_t – Concentration of the selected aniline derivative at time t (mM)

C_o – Concentration of the selected aniline derivative at time 0 (mM)

K – Pseudo-first order reaction rate constant (per minute)

t – time (minutes)

Regression analysis based on the pseudo-first order reaction kinetics were conducted for the degradation of individual aniline derivatives by Fenton's and photo-Fenton oxidation processes using $FeSO_4$ and Fe(LS) as catalysts. The values of pseudo-first order reaction rate constants and regression coefficients were obtained for each of the above mentioned processes.
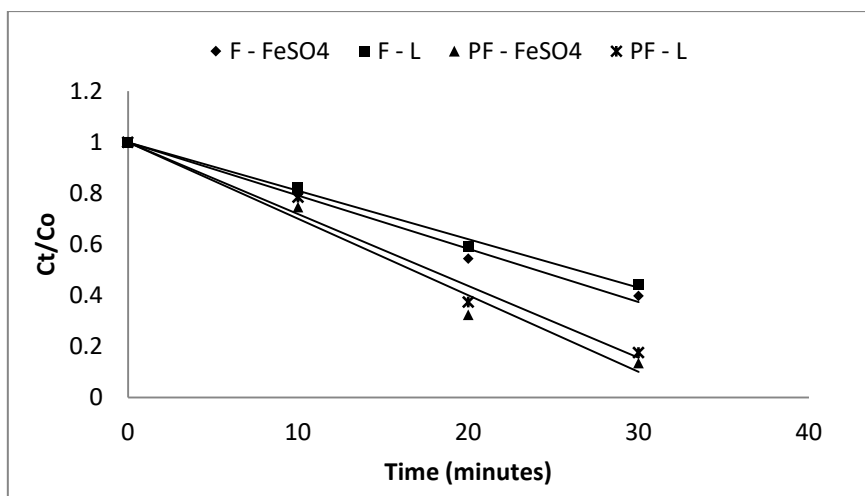
Figure 4.26: Kinetic profiles of 2-NA

Figure 4.26 shows the trends of a pseudo-first order reaction kinetic model for degradation of 2-NA by Fenton's and photo-Fenton processes. The kinetic study was conducted with an initial 2-NA concentration of 0.5 mM for optimum dosages i.e. hydrogen peroxide of 3.5 mM and iron concentration of 0.05 mM. The reaction rate constants and regression coefficients obtained for each process are given in Table 4.41.
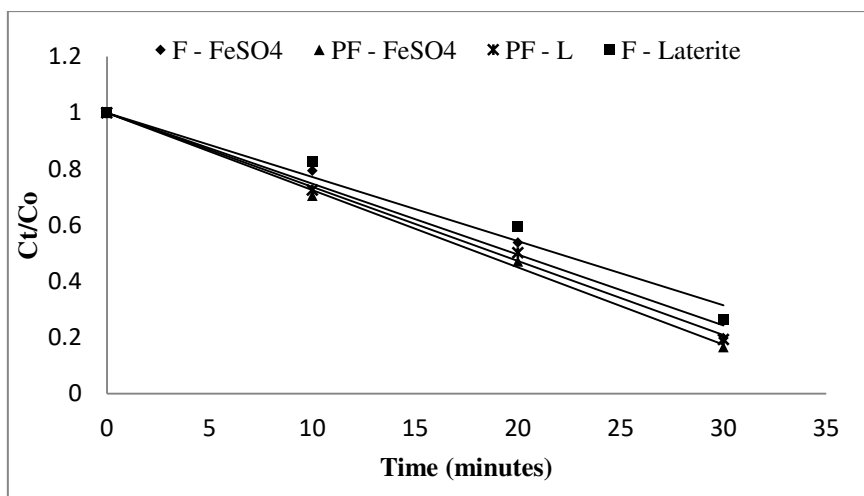
Table 4.41: Pseudo-first order kinetic constants for degradation of 2-NA

Process for degradation of 2-NA	Kinetic rate constant, K (minute⁻¹)		Regression Coefficient, R^2	
	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)
Fenton's oxidation	0.0209	0.019	0.9902	0.9941
Photo-Fenton Oxidation	0.03	0.0281	0.9804	0.9792

Figure 4.27 shows the trends of a pseudo-first order reaction kinetic model for degradation of 3-NA by Fenton's and photo-Fenton processes. The kinetic study was conducted with an initial 2-NA concentration of 0.5 mM for optimum dosages i.e. hydrogen peroxide of 4.5 mM and iron concentration of 0.05 mM. The reaction rate

constants and regression coefficients obtained for each process are given in Table 4.42.
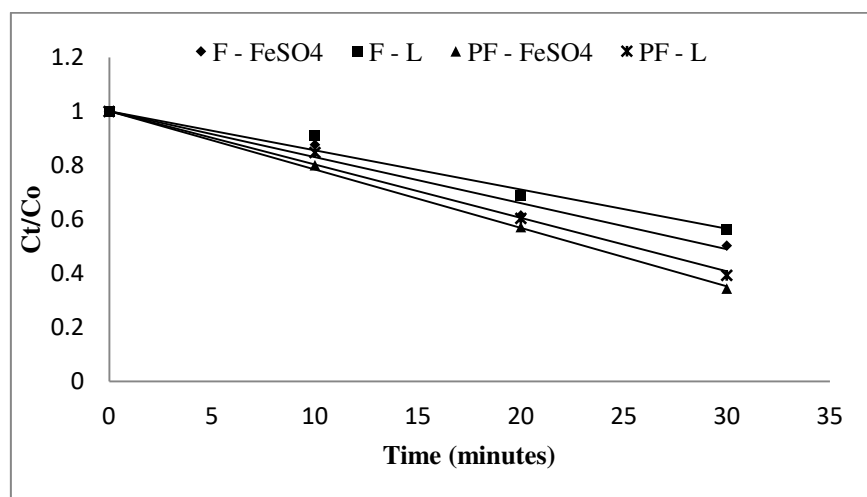
Figure 4.27: Kinetic profiles of 3-NA

Table 4.42: Pseudo-first order kinetic constants for degradation of 3-NA

Process for degradation of 3-NA	Kinetic rate constant, K ($minute^{-1}$)		Regression Coefficient, R^2	
	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)
Fenton's oxidation	0.017	0.0145	0.9721	0.97
Photo-Fenton Oxidation	0.0216	0.0198	0.9985	0.9894

The kinetic studies were carried out for 4-NA with 0.5 mM of initial concentration as shown in Figure 4.28. Optimum dosages of 5.0 mM hydrogen peroxide and 0.05 mM iron concentration were used. The reaction rate constants and regression coefficients obtained for each process are given in Table 4.43.
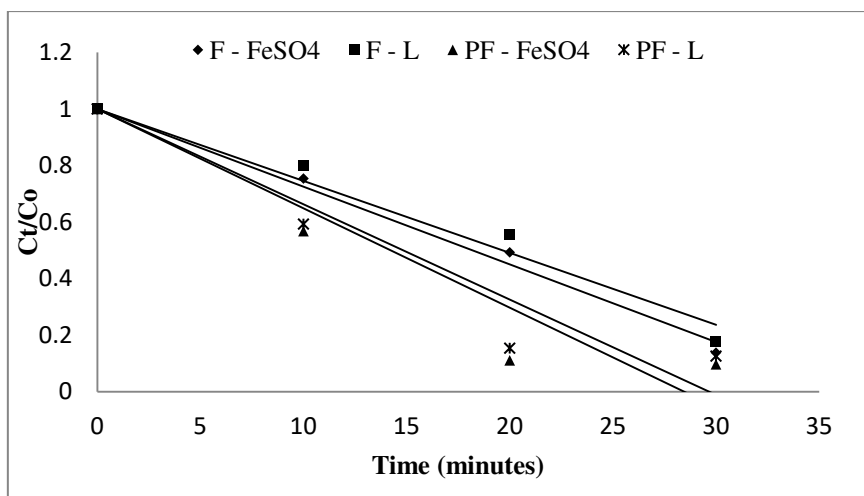
Figure 4.28: Kinetic profiles of 4-NA

Table 4.43: Pseudo-first order kinetic constants for degradation of 4-NA

Process for degradation of 4-NA	Kinetic rate constant, K (minute^{-1})		Regression Coefficient, R^2	
	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)
Fenton's oxidation	0.0275	0.0255	0.9901	0.9718
Photo-Fenton Oxidation	0.0351	0.0337	0.8848	0.8964

Figure 4.29 shows the kinetic profile of degradation of 2-MA which was carried out for the 0.5mM of initial concentration at optimum conditions of 3.5 mM hydrogen peroxide and 0.05 mM iron concentration. The reaction rate constants and regression coefficients obtained for each process are given in Table 4.44.
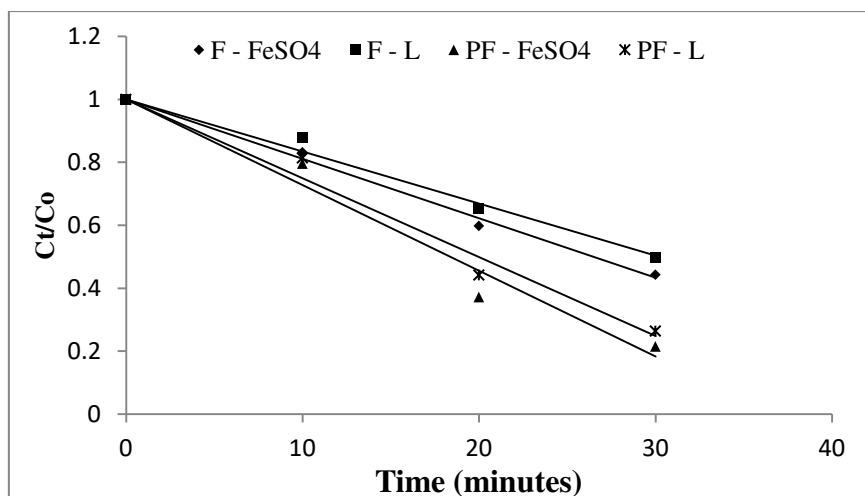
Figure 4.29: Kinetic profiles of 2-MA

Table 4.44: Pseudo-first order kinetic constants for degradation of 2-MA

Process for degradation of 2-MA	Kinetic rate constant, K (minute^{-1})		Regression Coefficient, R^2	
	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)
Fenton's oxidation	0.0189	0.0166	0.9939	0.9858
Photo-Fenton Oxidation	0.0273	0.0251	0.9683	0.9775

Figure 4.30 shows the trends of a pseudo-first order reaction kinetic model for degradation of 4-MA by Fenton's and photo-Fenton processes. The kinetic study was conducted with an initial 4-MA concentration of 0.5 mM for optimum dosages i.e. hydrogen peroxide of 5.0 mM and iron concentration of 0.05 mM. The reaction rate constants and regression coefficients obtained for each process are given in Table 4.45.

Figure 4.30: Kinetic profiles of 4-MA

Table 4.45: Pseudo-first order kinetic constants for degradation of 4-MA

Process for degradation of 4-MA	Kinetic rate constant, K (minute^{-1})		Regression Coefficient, R^2	
	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)
Fenton's oxidation	0.0253	0.0228	0.9833	0.9727
Photo-Fenton Oxidation	0.0275	0.0264	0.9975	0.9965

The experiments were carried out for a reaction time of 2 hrs. It is found that, rate of reaction decreases after 30 minutes. Hence the kinetics was studied for that time period.

The probable reason for the decrease in reaction rate at a later stage is that in the first stage ferrous ions react with hydrogen peroxide to produce a large amount of hydroxyl radical according to the following reaction.

$$H_2O_2 + Fe^{2+} \rightarrow\ ^\bullet OH + OH^- + Fe^{3+}$$
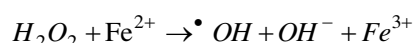
Further ferric ions produced in the first stage react with hydrogen peroxide to produce hydroperoxyl radicals (HO$_2$ $^\bullet$) and ferrous ions.

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+}$$

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$$FeOOH^{2+} \rightarrow HO_2{}^{\bullet} + Fe^{2+}$$
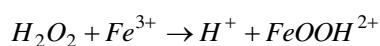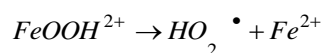
Thus hydroxyl radical and hydroperoxyl radicals are formed in the first and second stage, respectively. Oxidation capability of hydroxyl radical is much more than the hydroperoxyl radicals. The results obtained were consistent with those obtained in the study by Masomboon et al., 2011.

4.4 FENTON'S OXIDATION OF MIXTURE OF ANILINE DERIVATIVES

4.4.1 Fenton's oxidation of mixture of Aniline Derivatives using FeSO$_4$ as iron catalyst

The results presented earlier are with respect to the removal of individual aniline compounds. In the industrial wastewater, the aniline derivatives are in the form of a mixture of compounds. To treat this type of industrial wastewater it is necessary to have advanced process rather than the conventional wastewater treatment methods. In order to understand the synergetic or antagonistic effects, studies are conducted for the mixture of aniline compounds.

In the present study, a 1000 ml mixture of the five aniline derivatives was prepared. The initial concentration of each derivative was 0.5 mM. pH of the mixture was optimized at the beginning of the oxidation processes. Figure 4.31 shows the removal efficiencies obtained during pH optimization. The pH was varied from 2 to 4 by keeping the H$_2$O$_2$: Fe^{2+}:: 5: 0.05. The removal efficiency was maximum at pH 3. The 2-NA, 3-NA, 4-NA, 2-MA and 4-MA removal efficiencies obtained were 60.5%, 57.4%, 61.7%, 64.3% and 66.3 % respectively. Hence, for the further studies on the mixture of aniline derivatives pH 3 was considered optimum.
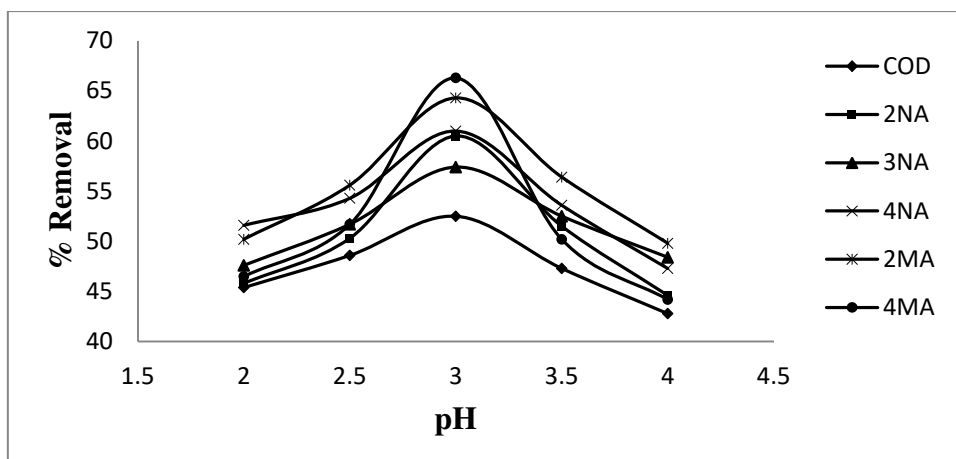
Figure 4.31: Effect of pH on removal of aniline derivatives in mixture of compounds (concentration: 0.5mM, H_2O_2 dosage: 5.0mM, Fe dosage: 0.05mM, Reaction Time = 5hrs)

To optimize the Fenton's dosages, experiments were conducted for 0.5 mM of aniline derivatives concentration by varying the hydrogen peroxide dosage from 5 mM – 19 mM, keeping the iron concentration constant as 0.05 mM. The maximum COD removal of 78.6% was observed at 17 mM of hydrogen peroxide concentration. The maximum 2-NA, 3-NA, 4-NA, 2-MA and 4-MA removal efficiencies obtained were 88.3%, 81.9%, 91.3%, 96% and 87.1% respectively at 17 mM of H_2O_2 concentration as shown in Figure 4.32.
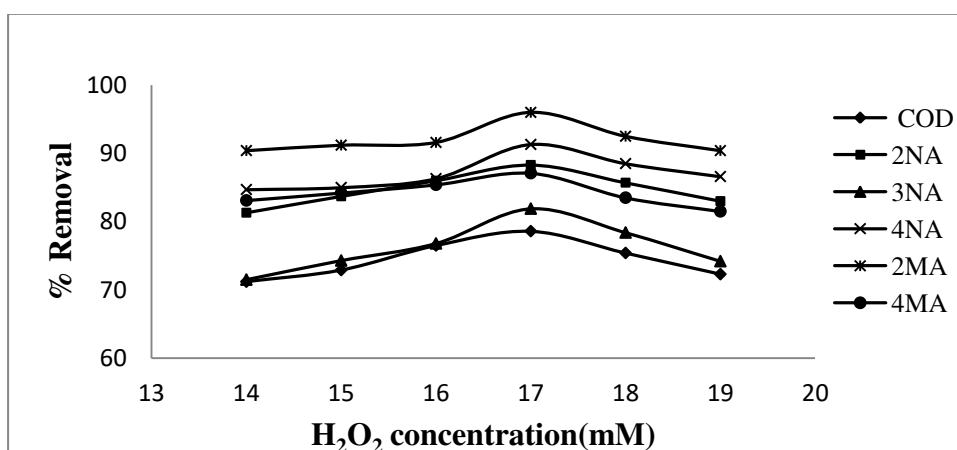
Figure 4.32: Effect of H_2O_2 concentration on removal efficiency in mixture of aniline derivatives (Concentration: 0.5mM, Fe dosage: 0.05mM, pH = 3.0, Reaction Time = 5hrs)

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Further, the Fe concentration was optimized by varying the Fe concentration in the range of 0.025 - 1.0 mM and keeping the hydrogen peroxide concentration as 17 mM. The maximum COD and respective compound removal efficiencies obtained at 0.05 mM of Fe concentration are as shown in Figure 4.33.
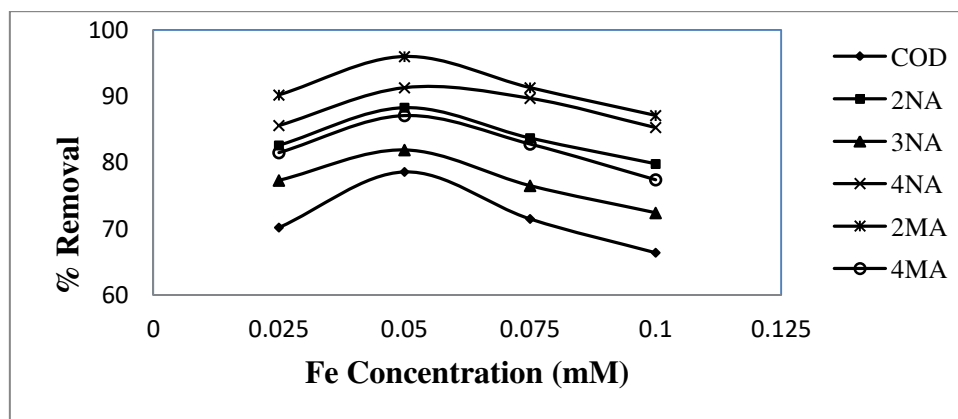
Figure 4.33: Effect of Fe concentration on removal efficiency in mixture of aniline derivatives (Concentration: 0.5mM, H$_2$O$_2$ dosage: 17.0mM, pH = 3.0, Reaction Time = 5hrs)

4.4.2 Fenton's oxidation of mixture of Aniline Derivatives using laterite iron as catalyst

The Fenton's oxidation has been carried out for a mixture of aniline derivatives using iron extracted from laterite soil as a source of iron. The experiments were carried out by varying H$_2$O$_2$ and iron concentration. Initially, a mixture of 0.5 mM concentration of each aniline derivative was prepared and pH of the mixture was adjusted to 3. The H$_2$O$_2$ dosage was varied from 5 mM – 19 mM and the removal efficiencies of each compound were measured using HPLC and COD removal efficiency was measured as shown in Figure 4.34. The removal efficiency of 2-NA, 3-NA, 4-NA, 2-MA and 4-MA obtained were 80.3 %, 76.2%, 82.7%, 88.8% and 81.6 % respectively. The maximum COD removal efficiency obtained was 72.4% at 17mM of H$_2$O$_2$ concentration.
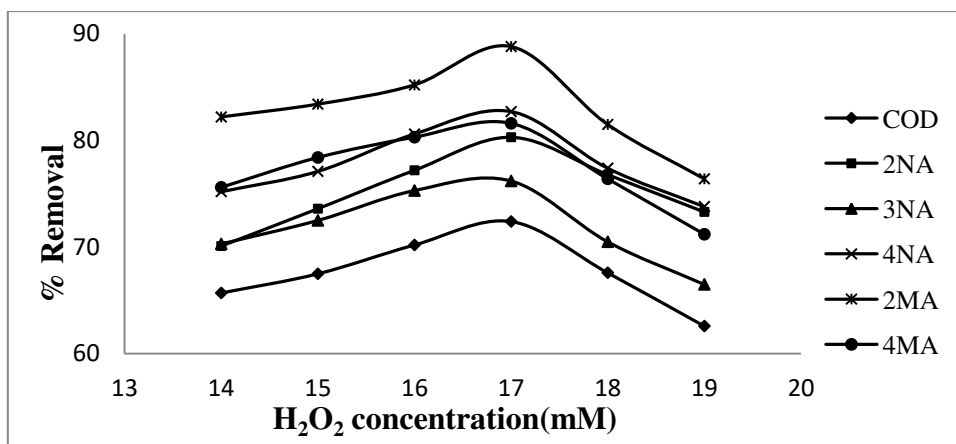
Figure 4.34: Effect of H_2O_2 concentration on removal efficiency in mixture of aniline derivatives (Concentration: 0.5mM, Fe (LS) dosage: 0.05mM, pH = 3.0, Reaction Time = 5hrs)

The iron extracted from laterite concentration was optimized by varying the concentration from 0.025 mM - 0.1 mM and the removal efficiencies obtained during experiments are as shown in Figure 4.35. The maximum removal efficiencies were obtained at 0.05 mM of iron concentration.
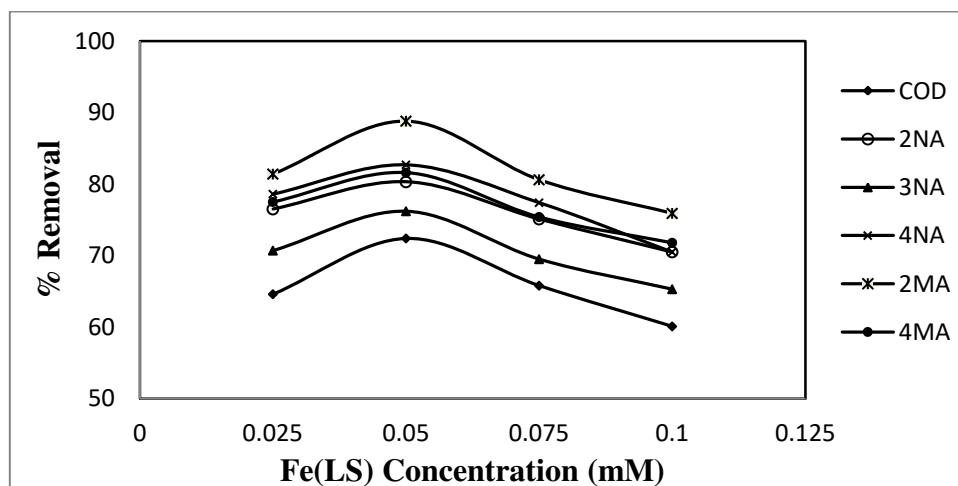
Figure 4.35: Effect of Fe (LS) concentration on removal efficiency in mixture of aniline derivatives (Concentration: 0.5mM, H_2O_2 dosage: 17.0mM, pH = 3.0, Reaction Time = 5hrs)

4.4.3 Photo-Fenton's oxidation of mixture of Aniline Derivatives

Photo-Fenton oxidation of aniline derivatives was carried out at the optimized dosages obtained during the Fenton's oxidation using $FeSO_4$ as a catalyst. The removal efficiency of 2-NA, 3-NA, 4-NA, 2-MA and 4-MA obtained during photo-Fenton oxidation are: 92.3%, 86.2%, 94.7%, 98.1%, 89.7% respectively and the COD removal efficiency obtained was 83.5%. The studies were further continued using iron extracted from the laterite soil as an alternative source of iron. The 2-NA, 3-NA, 4-NA, 2-MA and 4-MA removal efficiencies obtained are 85.7%, 80.4%, 86.9%, 92.6% and 85.4% respectively. The corresponding COD removal efficiency obtained was 76.8%. The removal efficiencies obtained during photo-Fenton oxidation using $FeSO_4$ as an iron source is slightly higher than the laterite iron as a source of iron.

4.5 DISCUSSIONS

The following section provides the possible explanation for the trends of experimental observations carried out in the present study. The present work, five different derivatives of aniline normally found in industrial wastewater have been chosen as a model compounds for the removal using Fenton and photo-Fenton oxidation and also replaced the conventional ferrous sulphate by iron leached out from laterite soil so as to economize the process. In the present study the effect of important parameters like pH, peroxide concentration, iron concentration, initial concentration of the compounds on the removal efficiency has been studied and optimized. Further as in the case of industrial wastewater mixture of compounds are normally present. The experimental results are also presented to understand the removal of individual compounds in the presence of other compounds. The kinetics of the reaction which has bearing on the design of reactor is also presented. In the set of results presented earlier, the effect of pH, H_2O_2 concentration, ferrous ion and replacement of ferrous sulphate by iron leached out from locally available laterite stones has been quantified and presented both in the form of tables and figures (The actual experimental results obtained have been confirmed by HPLC and UV-spectra).

4.5.1 Effect of pH

The pH plays an important role in the removal of specific aniline derivatives studied. It was observed that the removal efficiencies were maximum at pH 2.5 for 2-NA, 3-NA and 4-MA and pH 3 for 4-NA and 2-MA, and this can be explained by the following aspects of chemistry.

When pH is higher than optimum, ferrous ion catalyst gets deactivated and hence the production of hydroxyl radical considerably reduces leading to decrease in oxidation potential at the higher pH condition. The oxidation efficiency rapidly decreased, not only by decomposition of hydrogen peroxide but also by deactivation of a ferrous catalyst with the formation of ferric hydroxide complexes leading to a reduction of OH· radical. Hence results in the oxidation potential of hydroxyl radical were known to decrease with increase in the pH values (Lucas and Peres, 2006). Another reason for the inefficient degradation at pH>optimum is due to the dissociation and auto-decomposition of H_2O_2 (Badawy et al., 2006). For pH values below 3, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected causing the reduction in hydroxyl radical production. The low degradation is at pH 1 and 2 is due to the hydroxyl radical scavenging of H^+ ions (Lucas and Peres, 2006).

At lower pH conditions, pH< optimum, there is a possibility for the formation of oxonium ion ($H_3O_2^+$) due to the proton solvating ability of H_2O_2 and enhanced hydroxyl radical scavenging by H^+ ions. All the above facts results in reduce in the generation of OH radicals, there by leading to the decreased efficiency of the removal of aniline derivative compounds studied. The present results are in confirmation with the results reported in the literature by several authors (Sun et al., 2007, Kang et al., 2002). Other than that, one more possible explanation for the oxidation inhibition at pH lower than optimum is based on the main Fe^{3+} soluble species in equilibrium which shown in the equation below:

$$Fe^{2+} \rightarrow Fe^{3+} \Leftrightarrow Fe(OH)^{2+} \Leftrightarrow Fe(OH)^+_2$$

4.5.2 Effect of H_2O_2 concentration

It can be generally observed from the results presented earlier, that as the H_2O_2 concentration increases, generally the removal efficiency increases, but at higher concentration, it can be observed poor degradation. The experimental results confirm that there exists a critical concentration of H_2O_2 at which possibly the presence of hydroxyl radical is maximum. It is reported in the literature that beyond the critical concentration, the degradation rate of organic compound decreases with increases in the H_2O_2 concentration due to scavenging of the OH ions by H_2O_2 and incremental generation of OOH also consumes OH radical (Kang et al., 2002, Walling, 1975, Sun et al., 2007). The results obtained in the present study establish the critical concentration of H_2O_2 in the range of 3.5mM-5mM concentration for the different aniline derivative chemicals studied.

According to Hsueh et al., (2005) degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, with continuous increasing of the H_2O_2 concentration, the degradation rate of aniline derivatives reduced. This may be explained by the fact that the very reactive OH radical could be consumed by H_2O_2 and results in the generation of less reactive OOH radical (Chen and Pignatello., 1997; Kang et al., 2002; Walling and Kato., 1971, Muruganandham and Swaminathan, 2004.)

When a concentration higher than the critical concentration is used, the degradation rate of organic compounds was decreased as a result of so-called scavenging effect. As H_2O_2 concentration increase, reduction in the removal was also observed, which may be due to the hydroxyl radical scavenging effect of H_2O_2 according to Equation below:

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2{}^\bullet$$

$$HO_2{}^\bullet + {}^\bullet OH \rightarrow H_2O + O_2$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$$
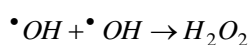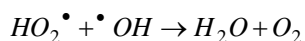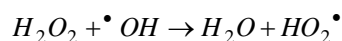
4.5.3 Effect of Fe^{2+} dosage

Ferrous ion is generally used as a catalyst which initiates the decomposition by H$_2$O$_2$, to generate the reactive OH ions in Fenton's reaction. Therefore normally it is expected the increase in the concentration of ferrous ion should generate higher OH ions and better degradation of chemicals. However, it can be observed from the results that, there is no significant impact of the ferrous concentration on removal efficiency. In the present study very low concentration of ferrous ion was used since higher dosage may require costly downstream process and also generate a huge quantity of ferric sludge.

The degradation efficiency of Fenton's process is also influenced by the concentration of Fe^{2+} ions which catalyse hydrogen peroxide decomposition resulting in OH radical production and consequently the degradation of an organic molecule. Further increase in iron concentration the degradation efficiency was reduced. Generally, with increasing ferrous salt concentration, the degradation rate of the organic compound also increases, but only to that certain level where the further addition of iron becomes inefficient (Tarr, 2003).

4.5.4 Effect of Initial concentration

The effect of initial concentration on Fenton's oxidation process was studied by varying the initial concentration of the pollutant concentration on all the model compounds selected. The removal of chosen model compounds and COD removal efficiency decreased with the increase in the initial concentration of the chosen model compounds.

This may be due to fact that, the requirement of OH radical increases with increase in the concentration and since the availability of the OH radical increases is lesser, the removal efficiency decreases with increases in the initial concentration (Sun et al., 2008) and the COD removal efficiency decreased at higher concentration may be because of the formation of the intermediates during Fenton's oxidation which traps OH radicals (Manu and Mahamood, 2011).

4-NA has got maximum removal efficiency of 98.7% among the nitro anilines degraded during Fenton's oxidation. This may be due to the fact that, anilines are ortho and para directing groups and hence degradation would be faster in case of 2-NA and 4-NA. However, when the nitro group is in ortho position, steric hindrance occurs between amine and nitro groups so degradation of 2-NA is slower compared to 4-NA. Hence, the 4-NA has more removal efficiency than 2-NA and 3-NA (Ahluwalia, 2010). Similarly, 4-MA has higher removal efficiency than 2-MA. It is also observed that removal of 4-NA is higher compared to that of 4-MA. This may be due to the steric hindrance caused by bulky alkyl group in methoxy anilines, which affects the substitution reaction. Hence, nitro anilines are more reactive than methoxy anilines. Similar trends were observed during Fenton's oxidation when laterite iron was used as a catalyst and also during the photo-Fenton oxidation.

The present study also has generated the results to obtain optimum H_2O_2 and optimum ferrous concentration at a different initial concentration of the aniline derivative chemical study. It can observed from the optimum conditions the ratio of peroxide to the iron concentration at optimum conditions is in the range of 70-110 indicating the requirement of a lower dosage of ferrous ion to generate the required quantity of OH radicals to obtain the maximum degradation efficiency. It was observed from the results, the removal efficiency decreased with the increase in the initial concentration of the aniline derivatives at a fixed ratio of peroxide to iron. However, the efficiency of removal increases at a higher ratio of peroxide to iron. It was observed from the results obtained that, As the H/F ratio increases the removal efficiency increases (Table 4.1) until it reaches an optimum value. The optimum H/F ratio increases with the increases in the initial concentration (Neyen and Baeyens, 2003).

Further, the major objective of the present study is to reduce the cost of advanced oxidation process by replacing the $FeSO_4$ by iron leached out with the laterite, a low cost locally available material. The results of the effect of iron from laterite on the degradation efficiency in comparison with $FeSO_4$ indicates that iron concentration of laterite could also reach maximum efficiency most similar. This

study has established that iron extracted from laterite may be used as an alternate to enhance the hydroxyl radical generation without much loss of efficiency of chemical removal.

4.6 CONCLUSIONS

- Among the compounds studied the maximum removal efficiency of almost 100% was obtained for 4-NA compound.

- The removal efficiency of the selected aniline derivatives in water follows the order: 4-NA>2-NA>3-NA and 4-MA>2-MA.

- The UV-C assisted photo-Fenton oxidation process has been proved much more efficient compared to conventional Fenton's oxidation process.

- Another important parameter established is the hydrogen peroxide/iron (H/F) ratio, which ranges from the 70-108 for the range of initial concentration studied (0.5 mM - 2.5 mM).

- The optimum hydrogen peroxide ranges from 3.5 mM to 5 mM and the optimum iron concentration as 0.05 mM for the different aniline compounds.

- The present study has established optimum pH for the Fenton's oxidation (2.5 and 3) for the different compounds.

- The present study has established that locally available laterite can generate enough hydroxyl radicals for use in Fenton's oxidation process.

- The iron extracted from locally available laterite soil used in the Fenton's oxidation process in the present study for the removal of different compounds of aniline could generate comparable removal efficiencies with that reported to be in the literature for the conventional process.

- The removal efficiencies for the mixture of aniline derivatives has been established in the present study.

4.7 FUTURE SCOPE FOR WORK

- Studies can be conducted to evaluate the effect of intensity of UV light on Photo Fenton oxidation of the aniline compounds.

- During the present study, the compounds degraded completely and simultaneously, there was a formation of other compounds, hence study on the by- products formed during the oxidation process may be quantified so as to explain the mechanism.

- The studies may be carried out for the actual wastewater from the industry in order to simulate the results obtained during the lab conditions.
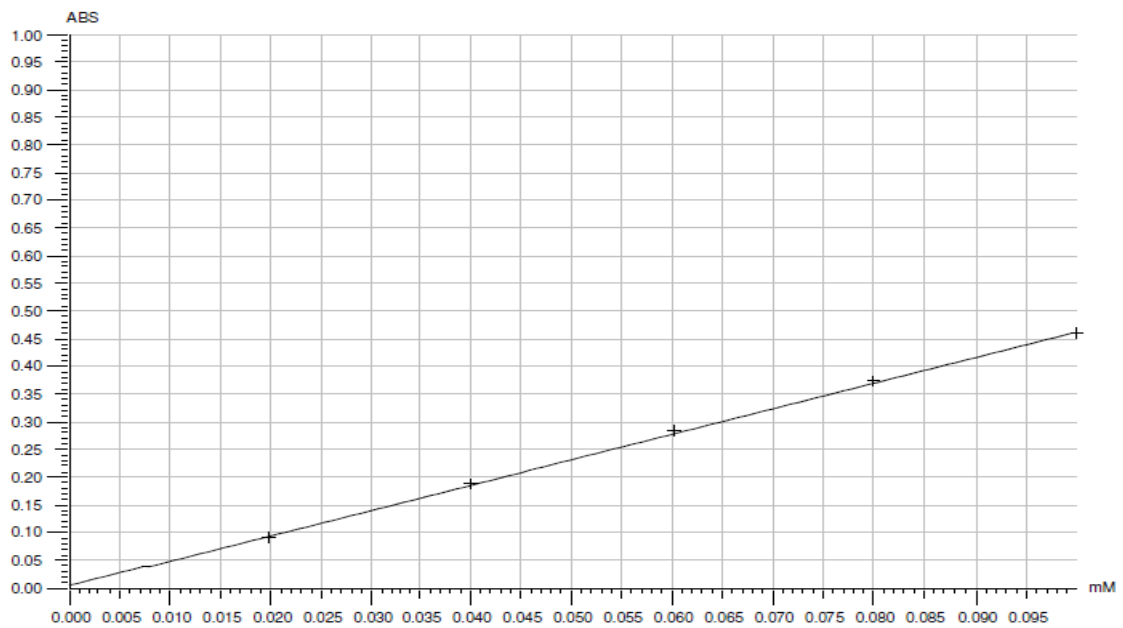
Figure A1: Calibration Curve of 2-Nitroaniline
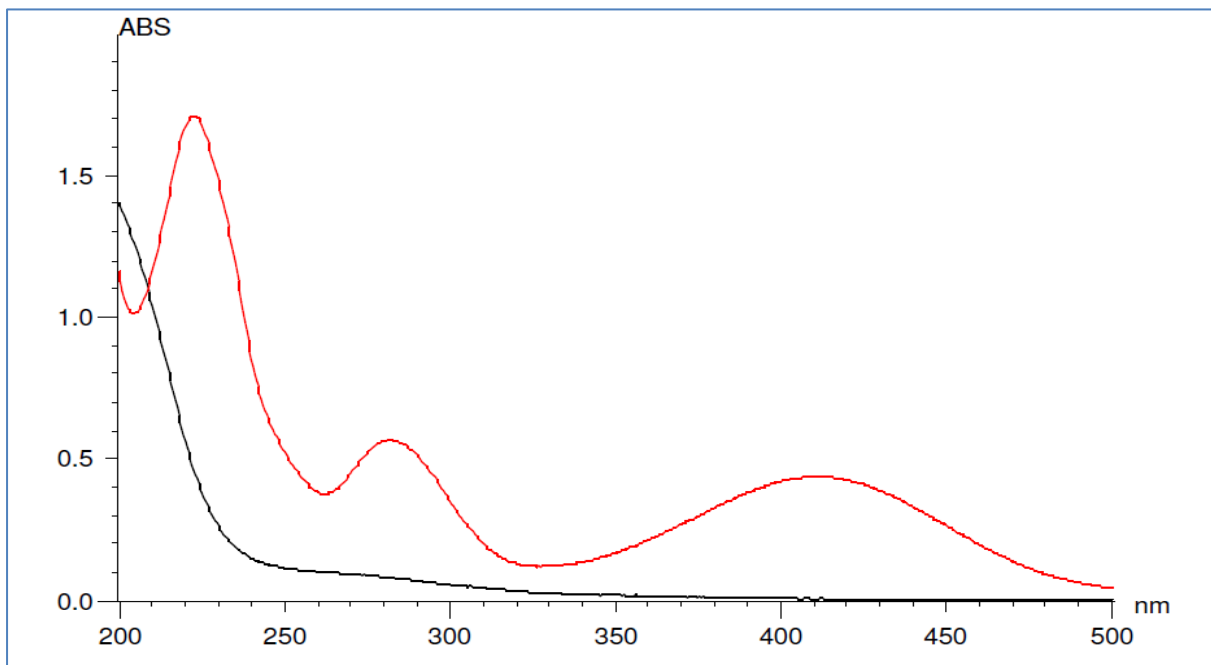
Figure A2: Before and after treatment scan of 2-Nitroaniline with optimal conditions (Concentration: 0.5mM, H_2O_2 dosage: 3.5mM, Fe dosage: 0.05mM pH = 2.5, Reaction Time = 5hrs)
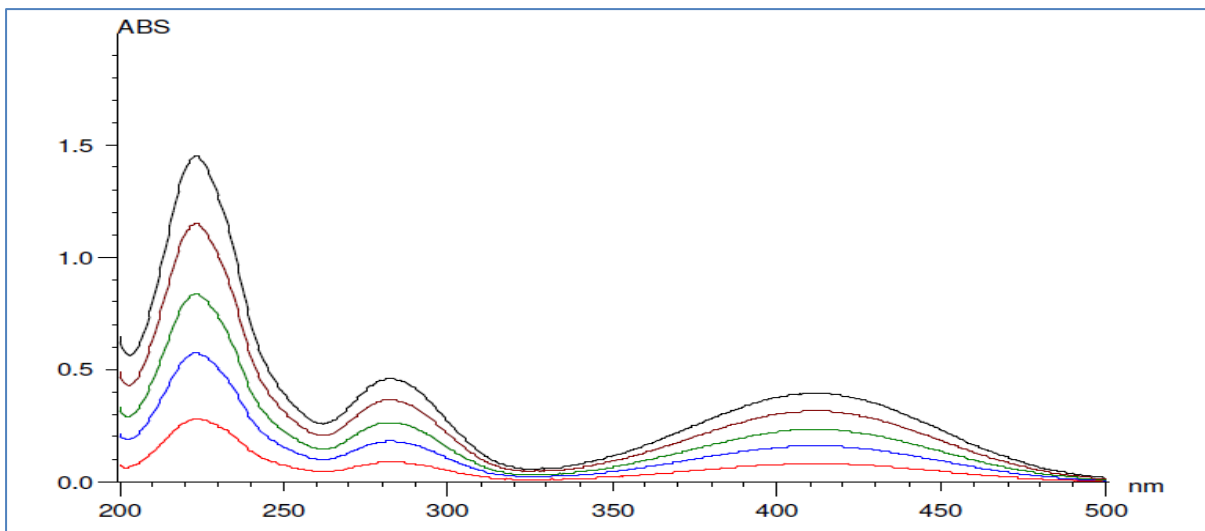
Figure A3: Before treatment scan of 2-Nitroaniline of 0.5-2.5mM initial concentration
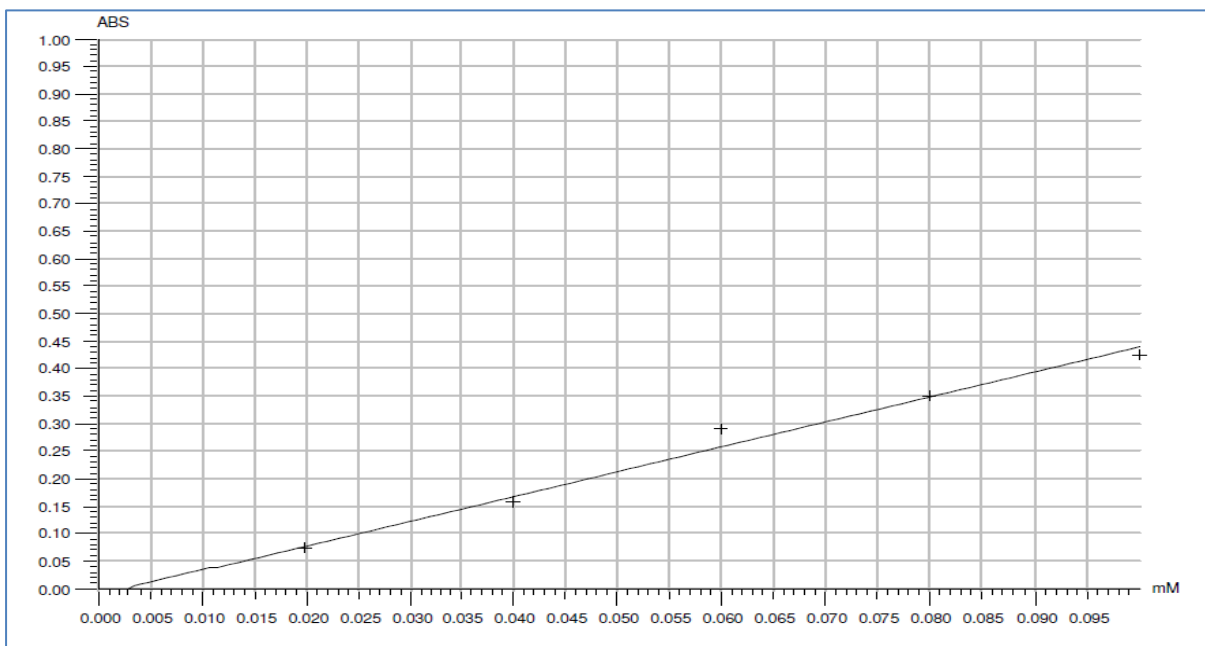
Figure A4: Calibration Curve of 3-Nitroaniline
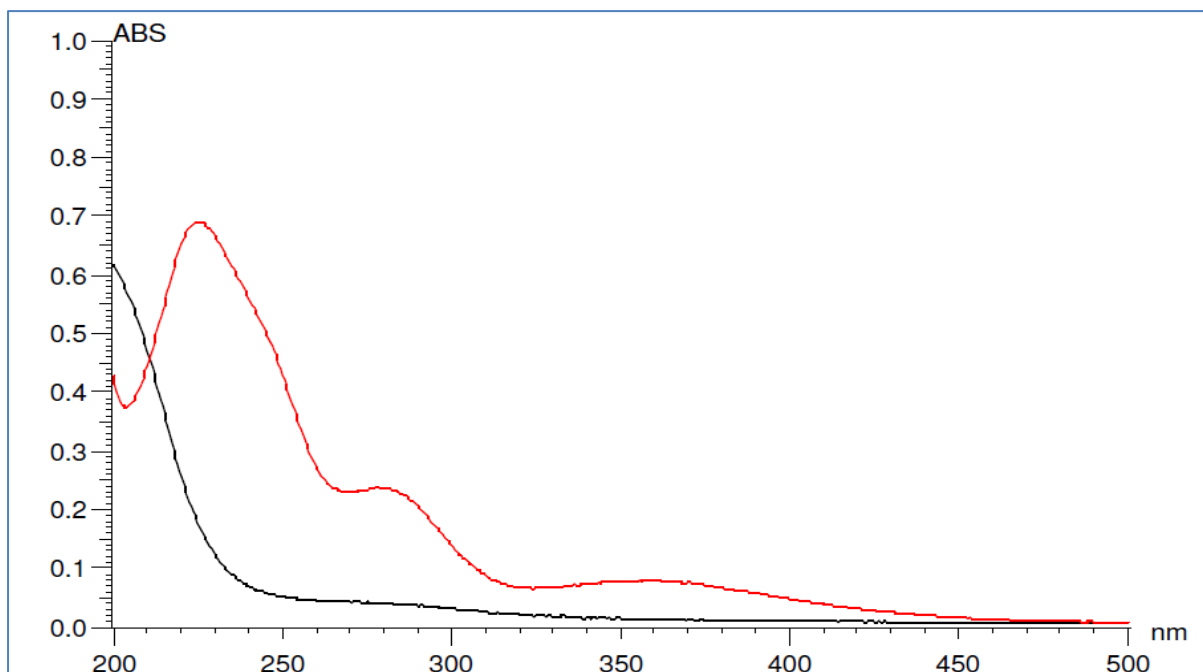
Figure A5: After treatment scan of 3-Nitroaniline with optimal conditions (Concentration: 0.5mM, H$_2$O$_2$ dosage: 4.5mM, Fe dosage: 0.05mM, pH = 2.5, Reaction Time = 5hrs)
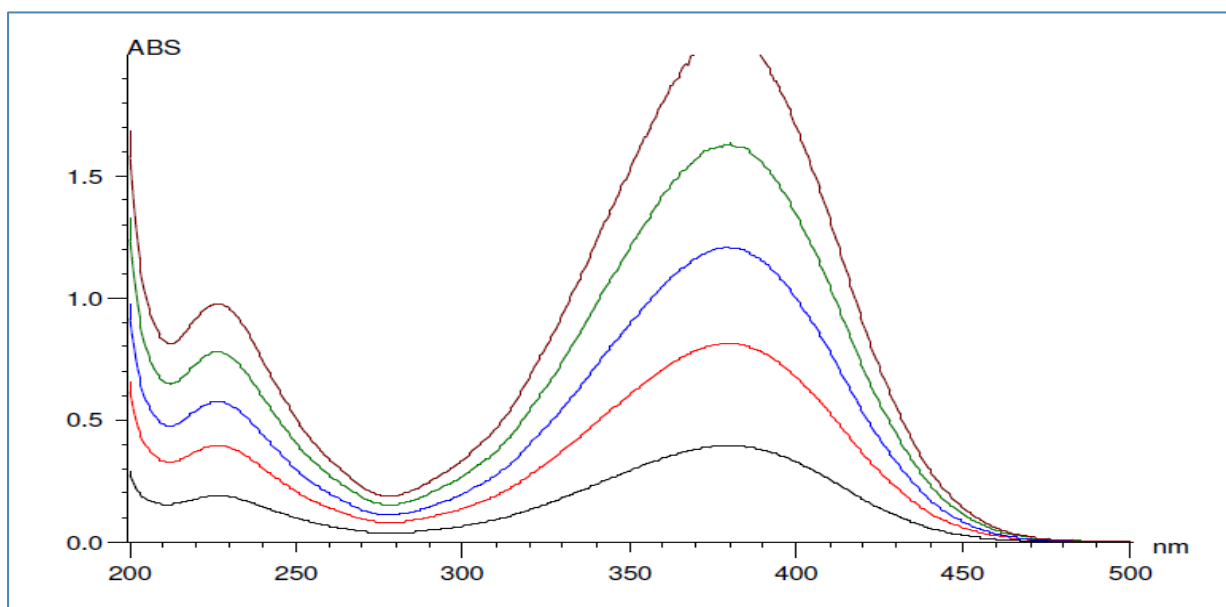
Figure A6: Before treatment scan of 4-Nitroaniline of 0.03-0.15mM initial concentration
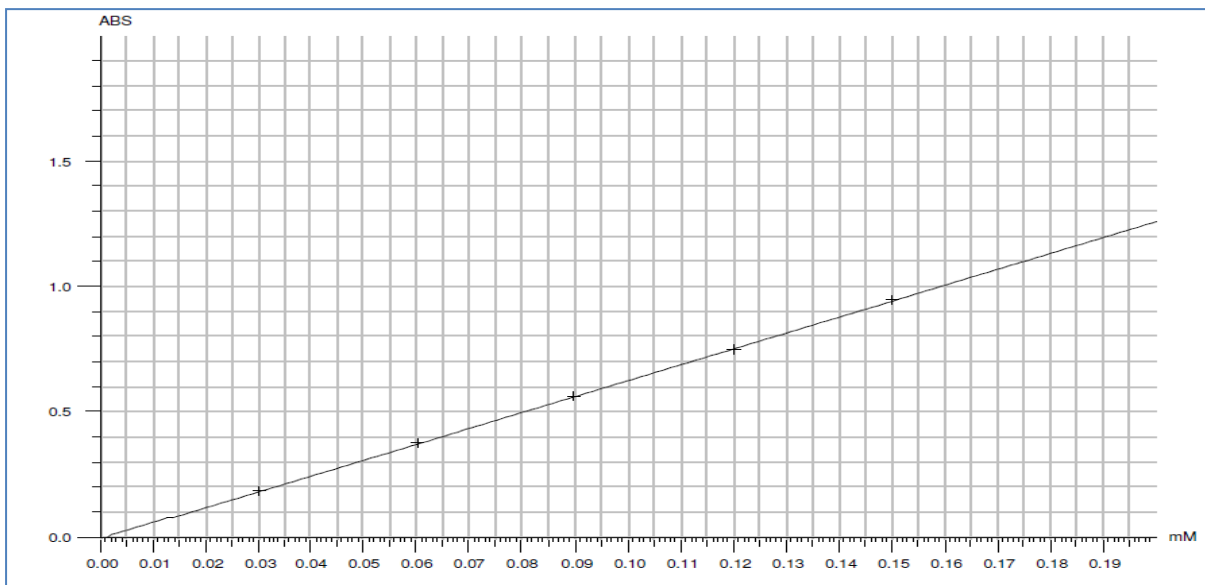
Figure A7: Calibration Curve of 4-Nitroaniline
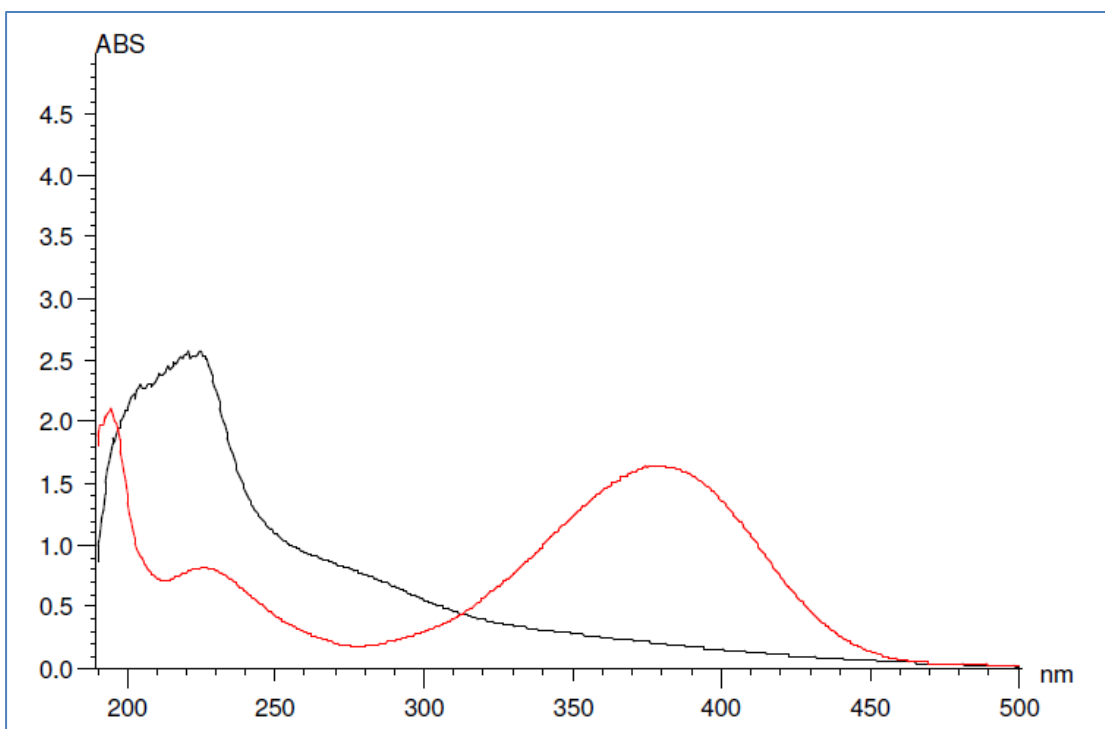
Figure A8: After treatment scan of 4-Nitroaniline with optimal conditions
(Concentration: 0.5mM, H_2O_2 dosage: 27mM, Fe dosage: 0.25mM pH = 3.0,
Reaction Time = 5hrs)
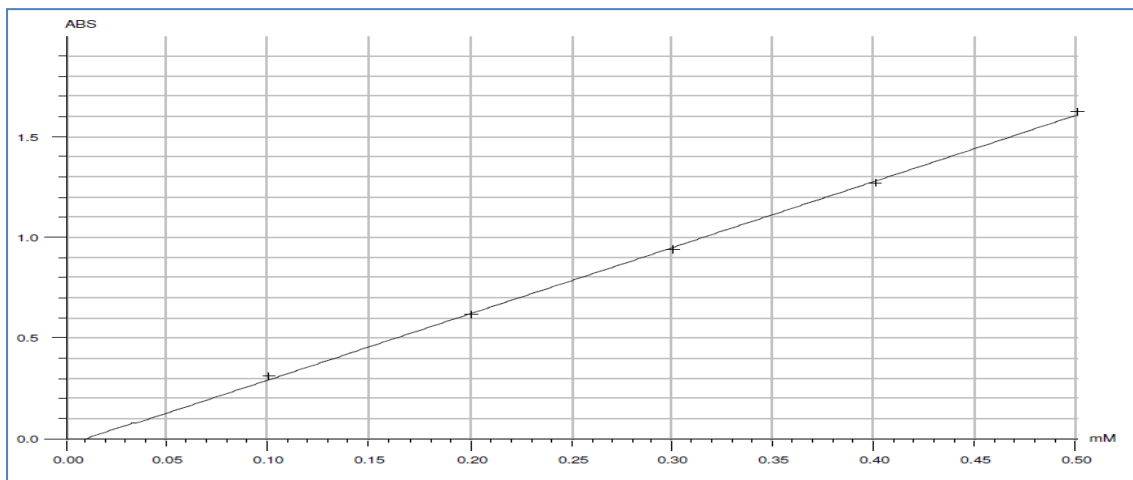
Figure A9: Calibration Curve of 2-Methoxyaniline
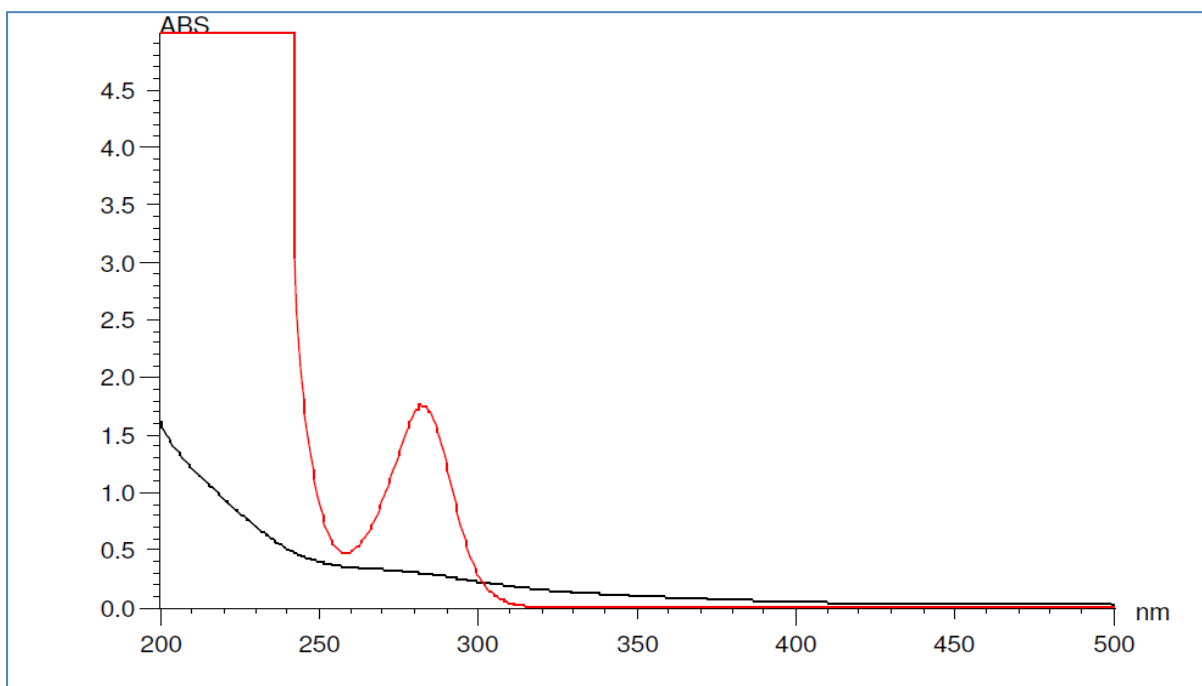
Figure A10: Before and after treatment scan of 2-Methoxyaniline with optimal conditions (Concentration: 0.5mM, H$_2$O$_2$ dosage: 3.5mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)
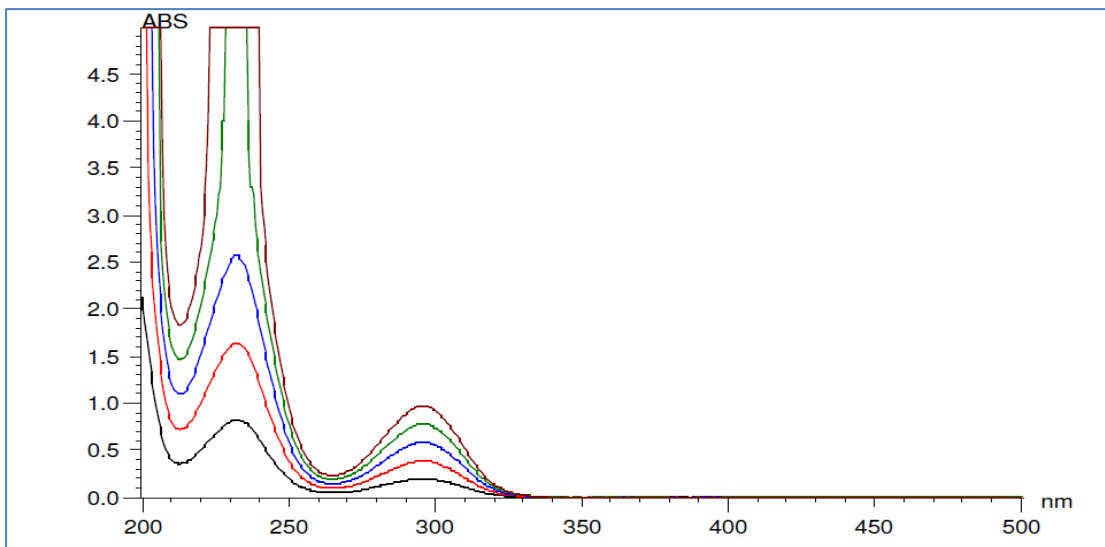
Figure A11: Before treatment scan of 4-Methoxyaniline of 0.5-2.5mM initial concentrations
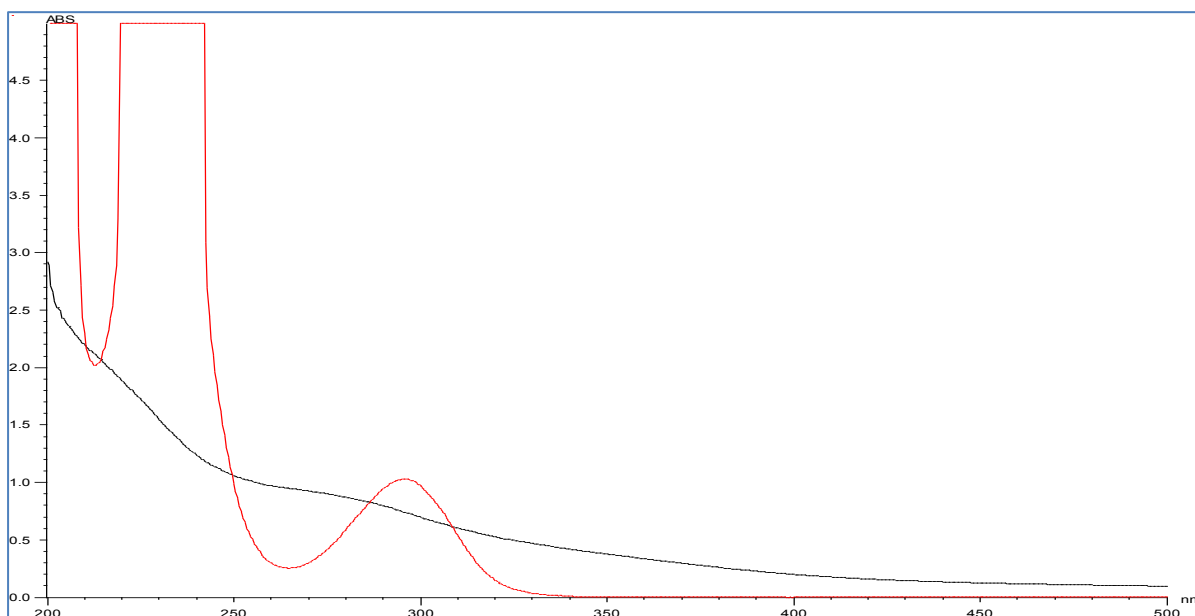
Figure A12: Before and after treatment scan of 4-Methoxyaniline with optimal conditions (Concentration: 2.0mM, H₂O₂ dosage: 21.5mM, Fe dosage: 0.2mM pH = 2.5, Reaction Time = 5hrs)
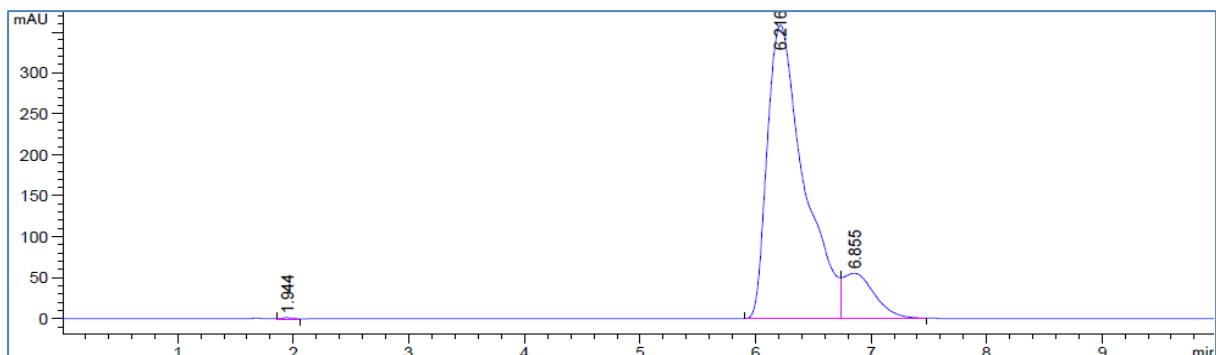
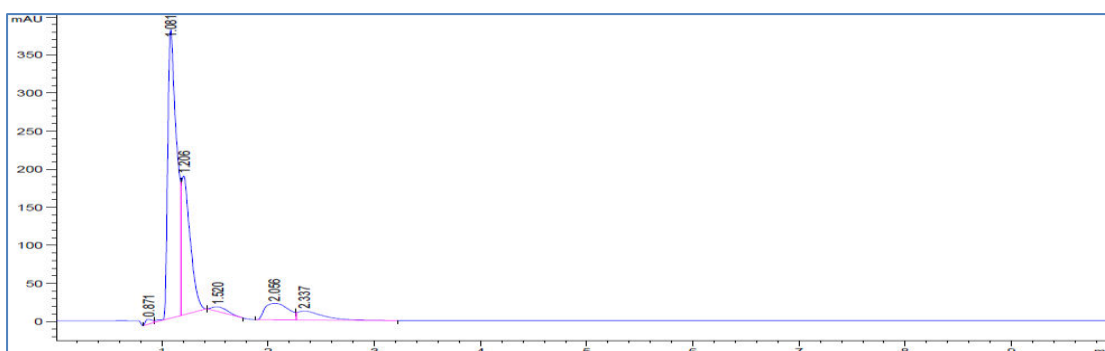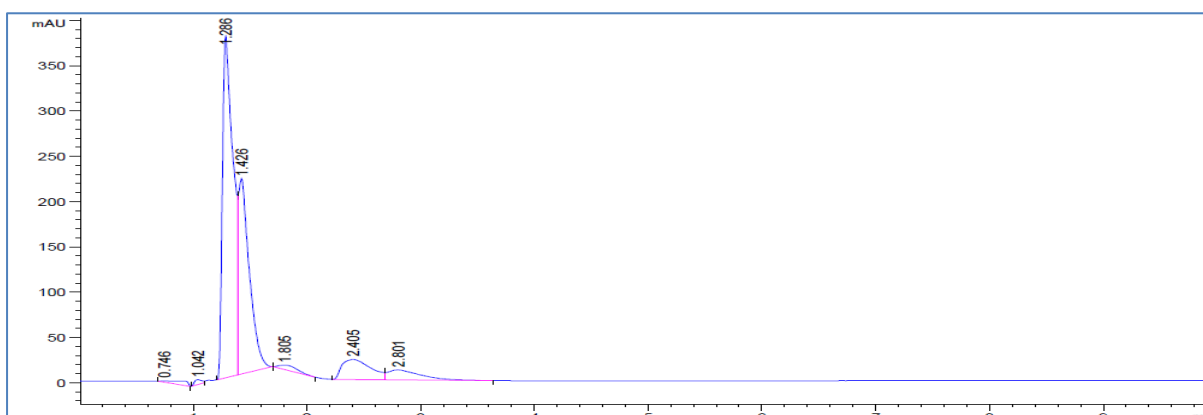**Figure A13: HPLC Chromatograph of 2-NA of 1.5mM concentration before Fenton's oxidation**
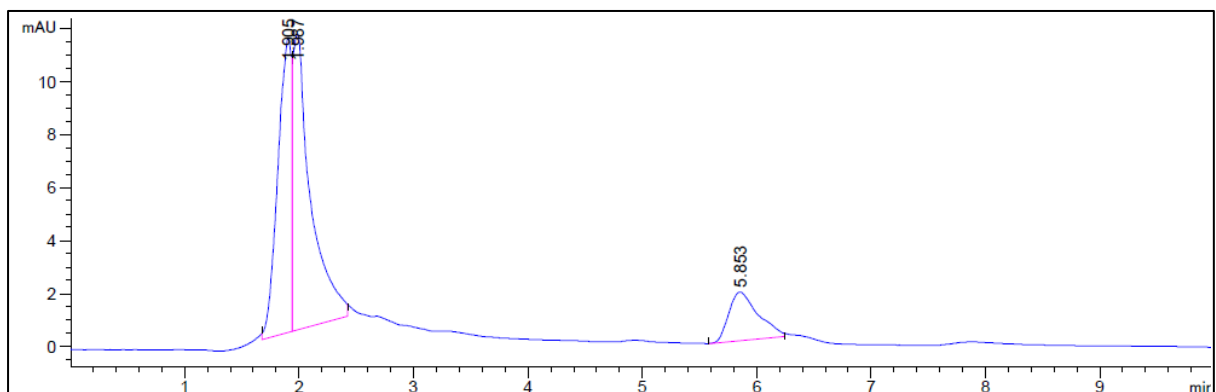
Figure A14: HPLC chromatograph of 2-NA of 1.5mM concentration at optimum conditions using FeSO₄ as catalyst (Concentration: 1.5mM, H₂O₂ dosage: 12mM, Fe dosage: 0.15mM pH = 2.5, Reaction Time = 5hrs)
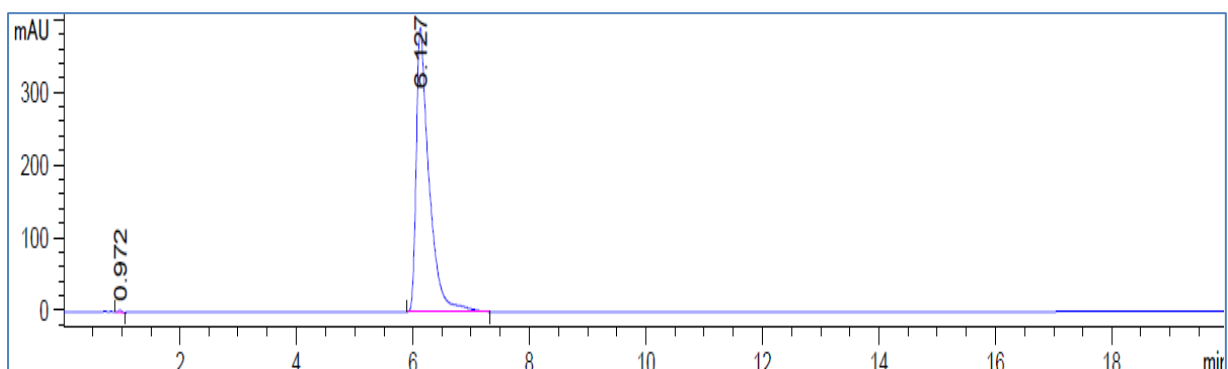
Figure A15: HPLC Chromatograph of 3-NA of 2.0mM concentration before Fenton's oxidation
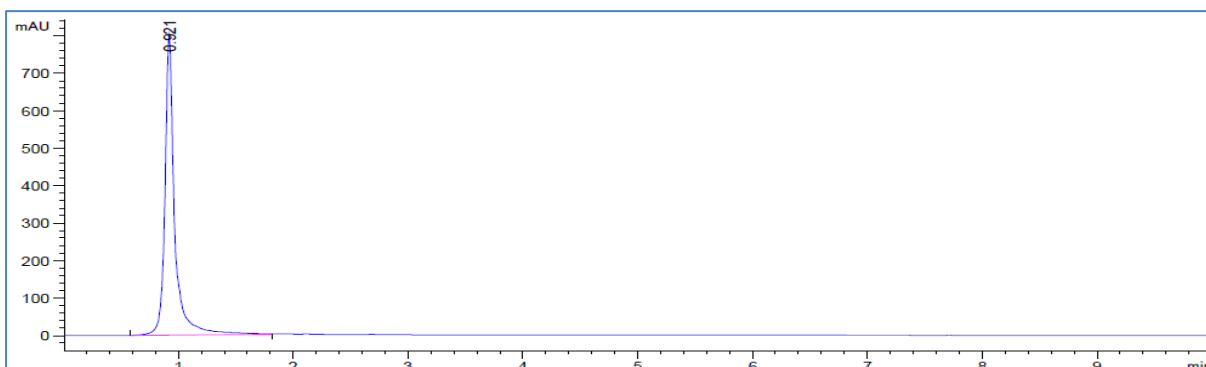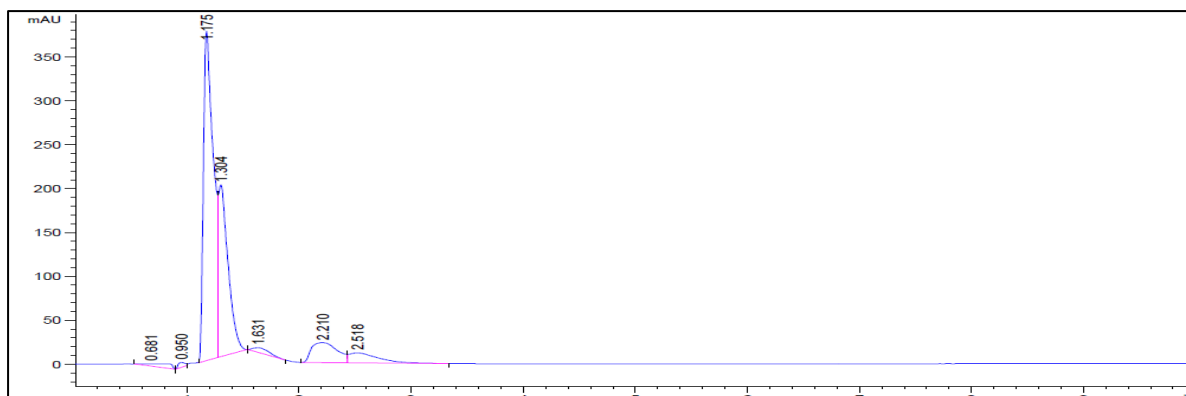
Figure A16: HPLC chromatograph of 3-NA of 2.0 mM concentration at optimum conditions (Concentration: 2.0mM, H_2O_2 dosage: 19.5mM, Fe dosage: 0.2mM pH = 2.5, Reaction Time = 5hrs)
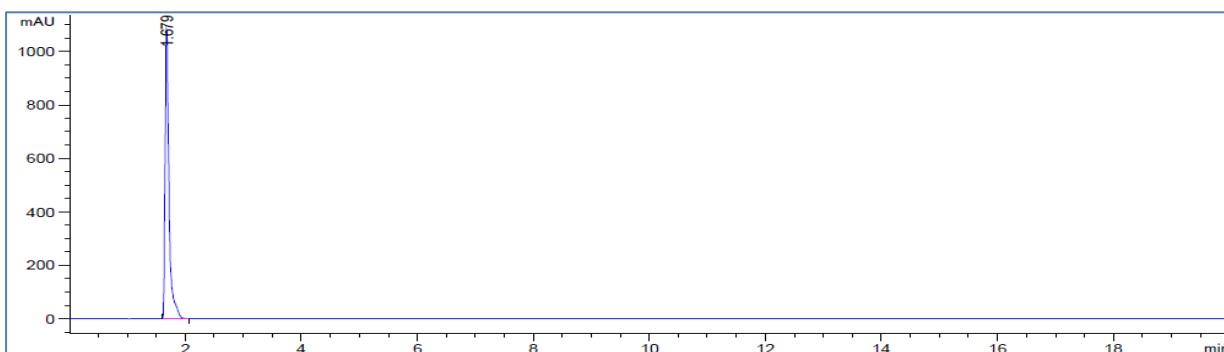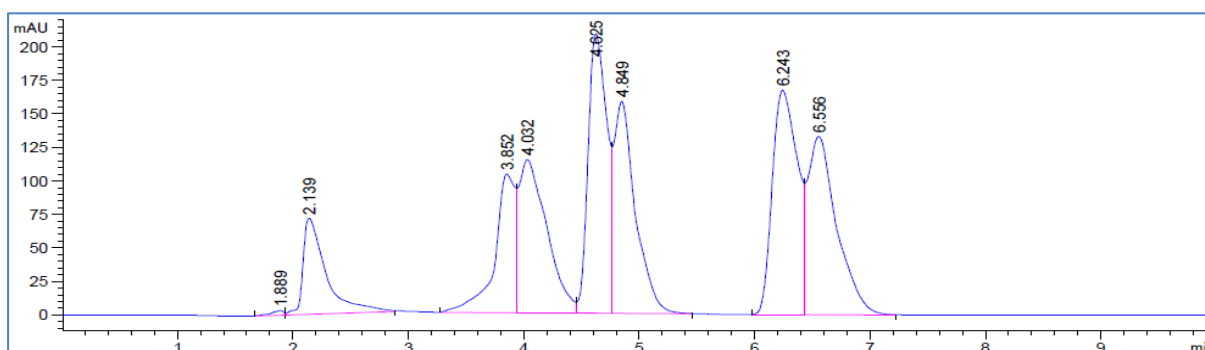

Figure A17: HPLC Chromatograph of 4-NA of 0.5mM concentration before Fenton's oxidation
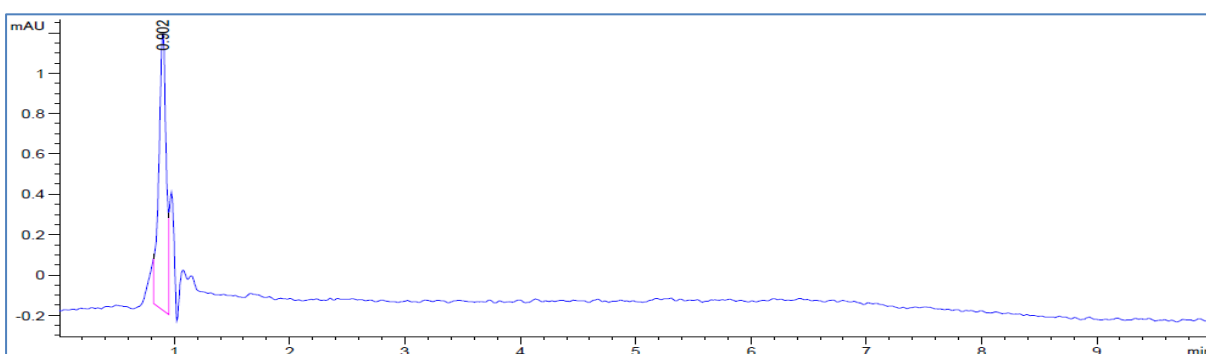
Figure A18: HPLC chromatograph of 4-NA of 0.5 mM concentration at optimum conditions (Concentration: 0.5mM, H_2O_2 dosage: 5.0mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)
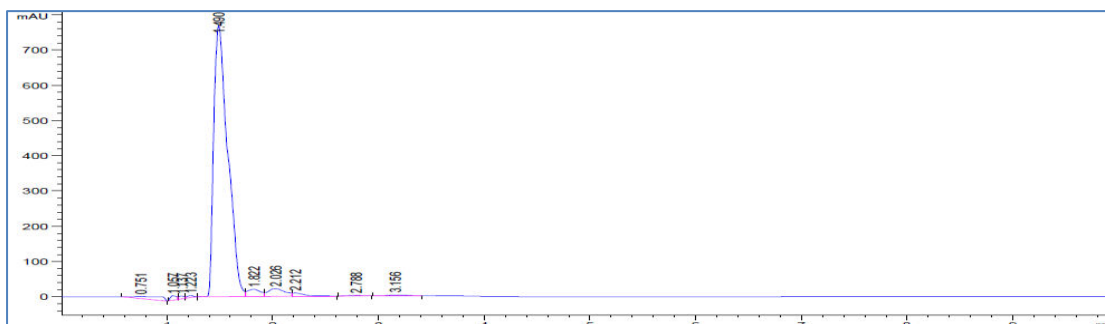
Figure A19: HPLC Chromatograph of 2-MA of 2.5mM concentration before Fenton's oxidation

Figure A20: HPLC chromatograph of 2-MA of 2.5 mM concentration at optimum conditions (Concentration: 2.5mM, H_2O_2 dosage: 19.5mM, Fe dosage: 0.25mM pH = 3.0, Reaction Time = 5hrs)

Figure A21: HPLC Chromatograph of 4-MA of 2.5mM concentration before Fenton's oxidation

Figure A22: HPLC chromatograph of 4-MA of 2.5 mM concentration at optimum conditions (Concentration: 2.5mM, H$_2$O$_2$ dosage: 27mM, Fe dosage: 0.25mM pH = 2.5, Reaction Time = 5hrs)
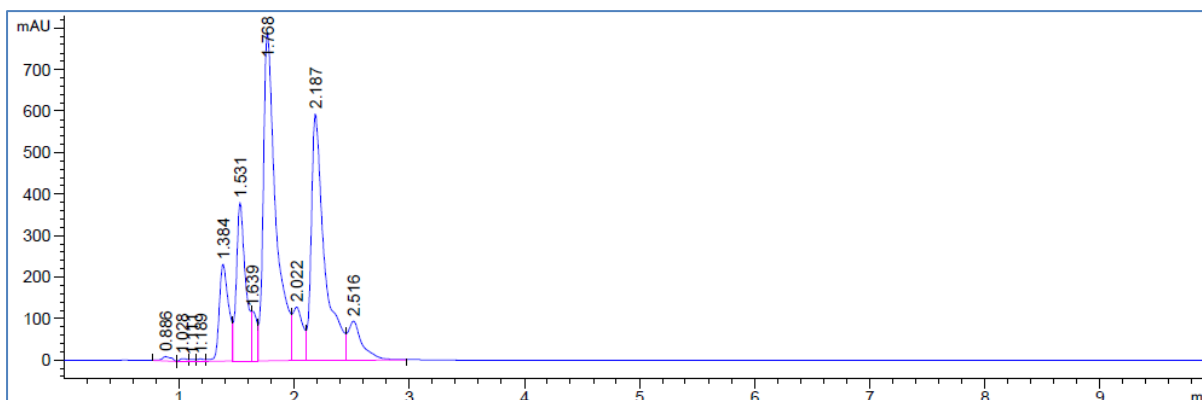

Figure A23: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration before Fenton's oxidation (2-NA method, λ_{max}= 282)
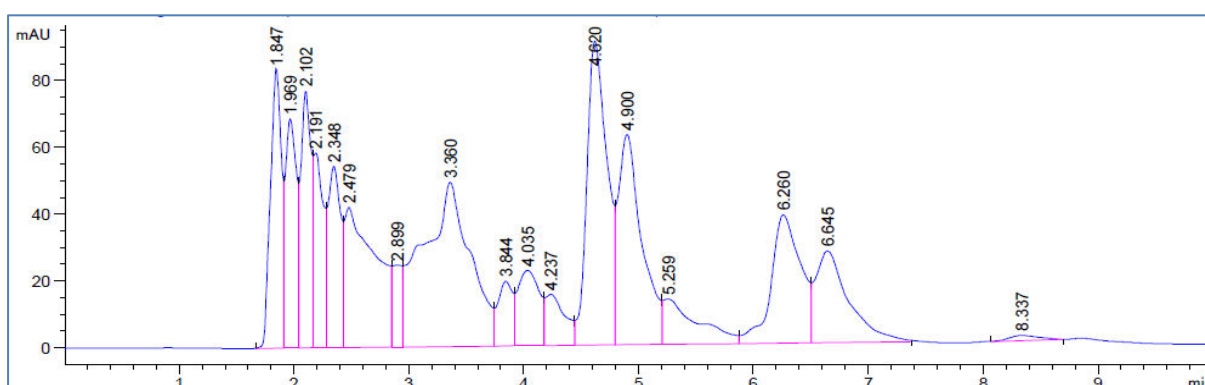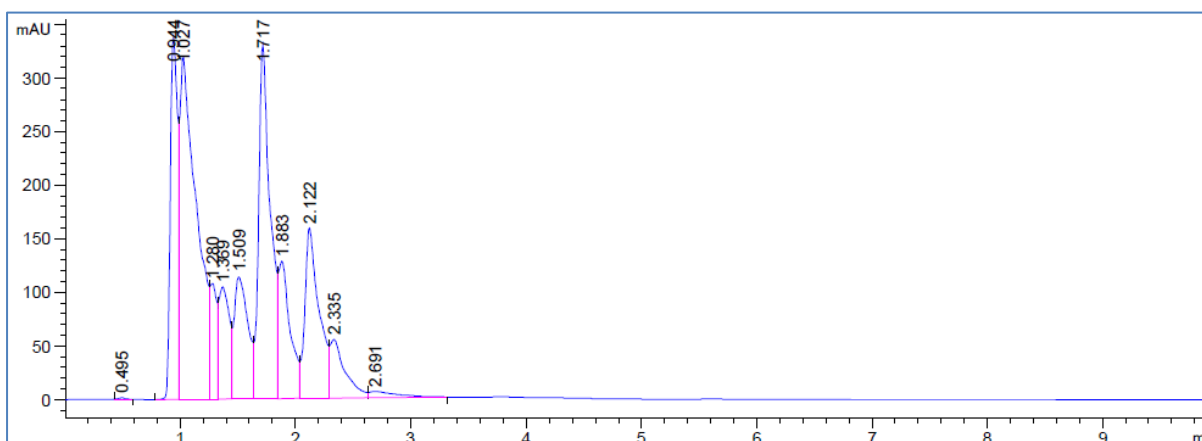

Figure A24: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration after treatment at optimum condition (2NA Method, H$_2$O$_2$ dosage: 17mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)

Figure A 25: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration before Fenton's oxidation (3NA method, λ_{max}= 227)

Figure A26: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration after treatment at optimum condition (3NA method, H_2O_2 dosage: 17mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)
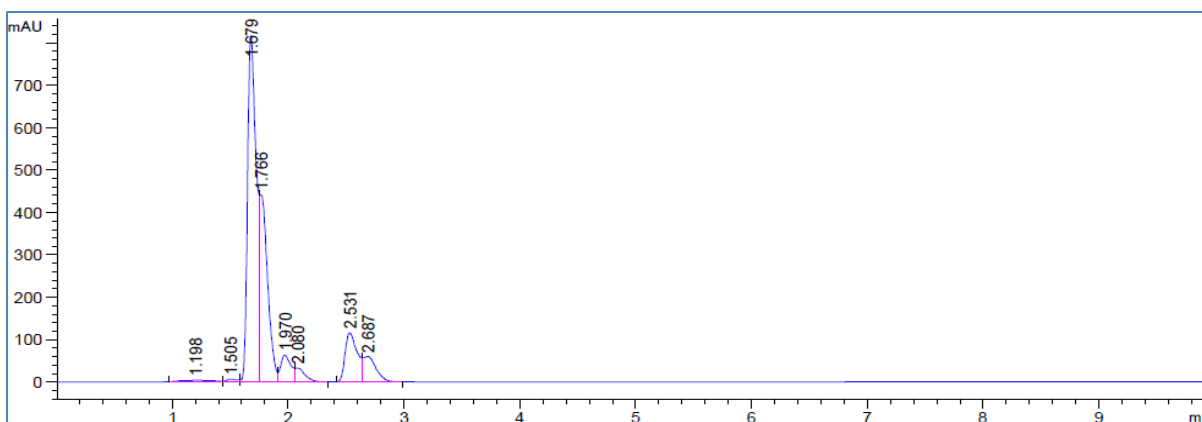

Figure A 27: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration before Fenton's oxidation (4NA method, λ_{max}= 380)
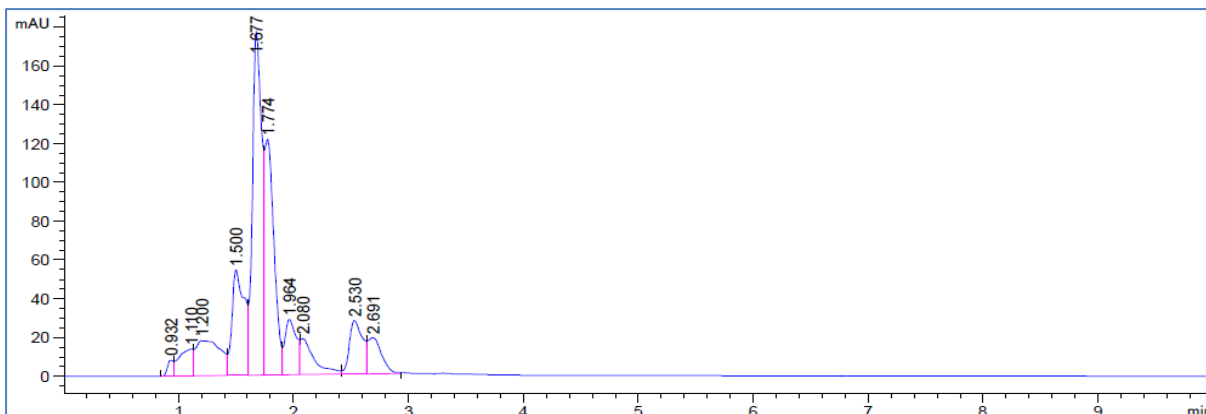
Figure A 28: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration at optimum condition (4NA method, H_2O_2 dosage: 17mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)
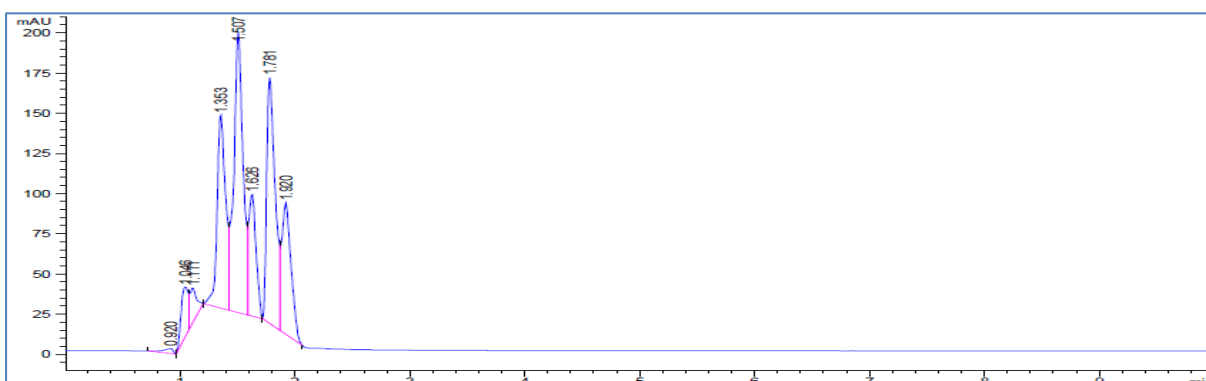

Figure A29: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration before Fenton's oxidation (2MA method, λ_{max}= 282)

Figure A30: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration after treatment at optimum condition (2MA method, H_2O_2 dosage: 17mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)

Figure A31: HPLC chromatograph of mixture of aniline derivatives of 0.5 mM concentration before Fenton's oxidation (4MA method, λ_{max}= 296)
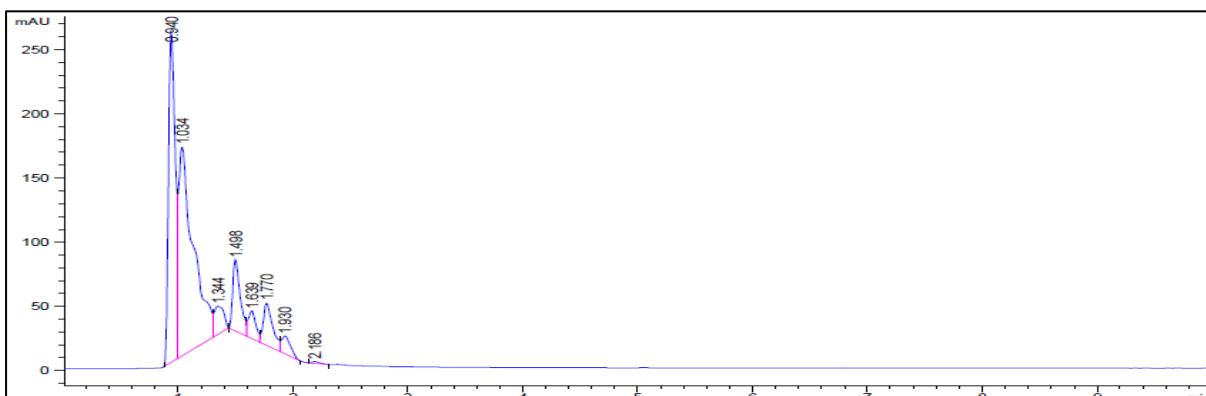

Figure A32: HPLC chromatograph of mixture of aniline derivatives of 0.5mM concentration after treatment at optimum condition (4MA method, H_2O_2 dosage: 17mM, Fe dosage: 0.05mM pH = 3.0, Reaction Time = 5hrs)
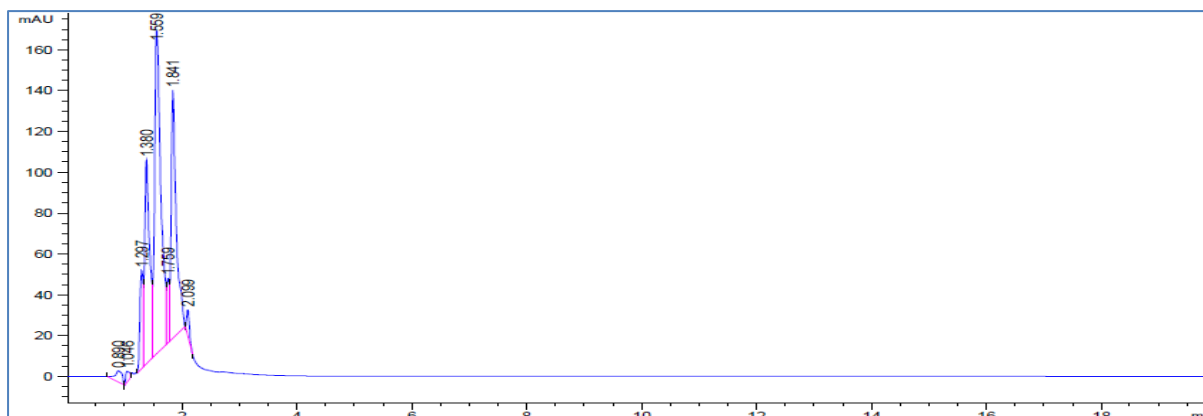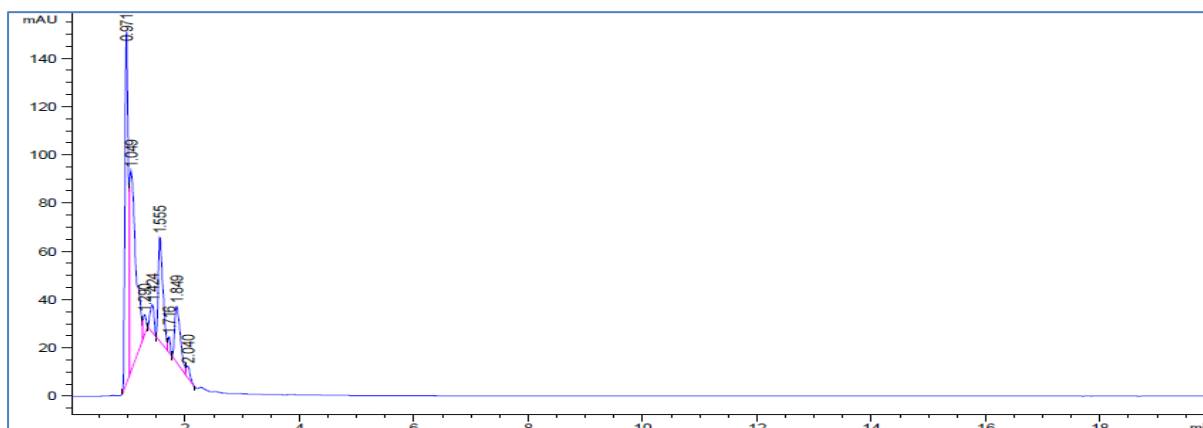
Table A1: Cost estimation of the Fenton's oxidation of the 2-NA

Particulars	Cost In Rupees	
	With FeSO$_4$.H$_2$O	With Laterite soil
H$_2$O$_2$	0.8	0.8
FeSO$_4$.H$_2$O	0.6	
HCl		0.4
H$_2$SO$_4$		
Power required for 5 hrs of agitation	4.0	4.0
Power required for iron extraction from laterite soil	-	0.08
Total	5.4	5.28

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