Degradation studies of herbicide isoproturon by using heterogeneous solar photo fenton process (using fly ash)

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Environmental Sciences and Technology

By

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DECLARATION & CERTIFICATE

I hereby declare that the work embodied in thesis entitled **"Degradation studies of herbicide isoproturon by using heterogenous solar photo fenton process (using fly ash)"** for the award of degree of Master of Technology (EST) submitted in the **School of Energy and Environment,** Thapar University, Patiala on July 2013, is a record of the work carried out by me under the guidance of **Mr. Anoop Verma** Assistant Professor, School of Energy and Environment. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

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It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

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ABSTRACT

Pesticides carried over in surface waters and groundwater raise serious environmental concerns due to hazardous and bio cumulative affects that may impose to living organisms. In this respect, abatement of pesticide-induced micro-pollution requires the development of efficient technologies capable of dealing with toxic and bio recalcitrant species present at very low concentrations. Over the past few years, various AOPs have indeed been tested extensively for the degradation of several classes of pesticides. The incapability of conventional biological wastewater treatment to effectively remove many industrial toxic pollutants shows that new treatment systems are needed. Advanced oxidation processes can be used to treat pesticides but they are expensive so we can make them cost effective by using waste material as an alternate source of catalyst. In this context, fly ash can be used as iron source in photofenton reaction. Fly ash is a waste material originating in large quantities from modern power stations. Although it has been successfully used as a mineral admixture in concrete and brick production, there are still superfluous fly ashes in some countries, causing environmental and disposal problem. The utilization of fly ash for industrial wastewater treatment could be rewarding to both environment and economy. In our present studied we focus on use of fly as a catalyst in Fenton reaction which along with H_2O_2 helps in degradation of non biodegradable herbicide isoproturon. Experiments were performed in dark , UV light and sunlight to check the efficiency of the process. The effect of fly ash dosage , amount of H_2O_2, pH, initial concentration of isoproturon were studied. Solar photo fenton method was found to be effective and could yield better results than either UV fenton or dark fenton. Degradation of 92.2% was observed under optimum conditions (dosage of fly ash 1gm; H_2O_2 10mM; pH 2). Recycling studies were performed by separating the used fly ash from the system and little decrease in efficiency of fly ash was observed due to surface fouling. Actually metal oxide compounds in fly ash, such as iron and manganese, can combine with H_2O_2 to form a Fenton-like reagent and produce hydroxyl radical, which can oxidize persistent organic pollutants into small molecule compounds.

Keywords: Advanced oxidation processes (AOP), Isoproturon, solar photofenton process, Fly ash.

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Chapter 1

Introduction

One of the main current worldwide concerns is the growth of surface and groundwater pollution. In particular, water contamination by pesticides is a severe problem. The risk inherent to pesticide pollution is prominent due to their generally high solubility in water, low-sorption affinity to soils, toxicity, chemical stability, bioaccumulation and low biodegradability **(Zapata A. et al., 2009)**. The major sources of pollution by pesticides are drainage waters from intensive agriculture, including water from washing pesticides containers and application equipment, and effluents from agricultural industries and pesticide manufacturing plants **(Ballesteros M.M. et al., 2009; Malato S. et al., 2000)**. EU legislation is being continually updated to protect and improve water quality, as is the case of Water Framework Directive (WFD), which establishes the guidelines for community action in the field of water policy **(Directive 2000/60/EC of the Council, 2000)**. A list of 33 Priority Substances, which represent a significant risk to or via the aquatic environment, including pesticides (alachlor, atrazine, chorfenvinphos, chlopyrifos, diuron, endosulfan, isoproturon, hexachlorocyclohexane, pentachorophenol, simazine and trifluraline) was later defined by the European Commission **(Directive 2000/60/EC of the European Parliament and of the Council, 2008)**. The incapability of conventional biological wastewater treatment to effectively remove many industrial toxic pollutants shows that new treatment systems are needed.

In the European Union, water policy is undergoing considerable changes at present. The adoption of the Framework Directive on water (**European Commission, 2000**) provides a policy tool that enables this essential resource to be sustainably protected. Among other measures, surface water deterioration must be prevented by reducing pollution from discharges and emissions of hazardous substances by 2015 **(European Commission, 2002)**. Thermal treatments present considerable emissions of other hazardous compounds, and separation treatments, require post-treatment. Alternative methods to these well-established techniques involve the oxidation of pollutants with reagents such wet oxidation, potassium permanganate, hydrogen peroxide and ozone **(Gogate and Pandit, 2004)**. Among these techniques, the so-called advanced oxidation processes (AOPs) appear to be a promising field of study. These techniques (H_2O_2+UV, O_3+UV, H_2O_2+O_3, photo-Fenton,

TiO_2–UV, etc.) can provide the conversion of contaminants to less harmful compounds **(Konstantinou and Albanis, 2004**).

Advanced Oxidation Processes (AOPs) are chemical oxidation techniques able to produce in situ free radicals , mainly the hyrdoxyl radical (OH*), by means of different reacting systems. The concept was originally established by **(Glaze et al**., **2000)** as "oxidation processes which generate hydroxyl radical in sufficient quantity to affect water treatment. They mainly rely on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radicals (OH*). Fig 1.1 shows different advanced oxidation processes

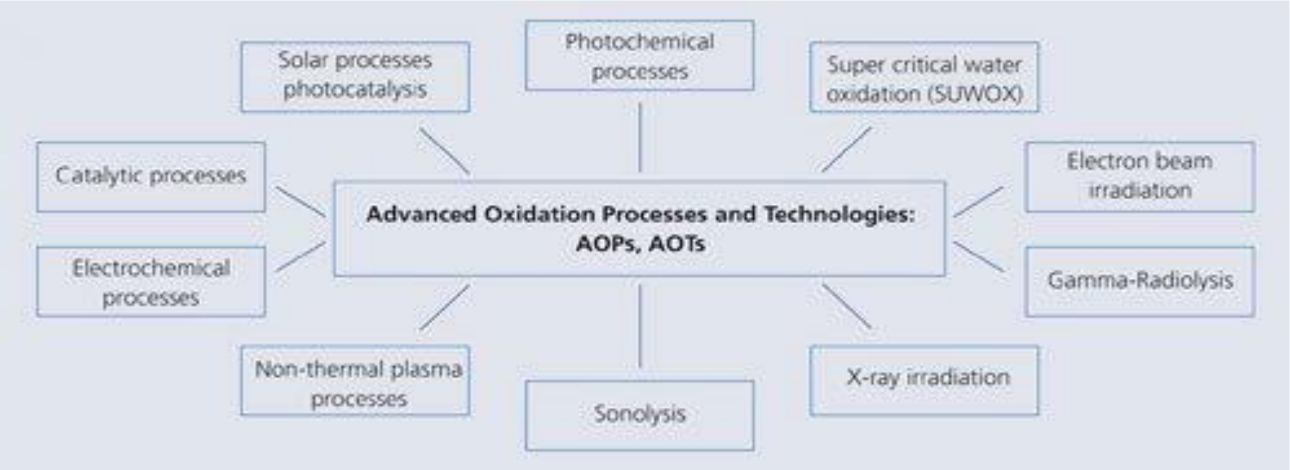


Fig (1.1) Different advanced oxidation processes

Among the different approaches used to achieve pesticide elimination, and considering their bio-recalcitrant character, advanced oxidation processes (AOPs) have been recognized as especially efficient when compared to conventional technologies **(Devipriya S. et al., 2005; Gogate P.R.et al., 2004)**. AOPs are chemical oxidation processes characterized by the production of extremely reactive and unselective oxidants, mostly hydroxyl radicals (HO*). They are able to oxidize and mineralize almost any organic compound, even bio-recalcitrant ones. AOPs' versatility is enhanced by the fact that there are many different ways of producing HO*. Heterogeneous photocatalysis using titanium dioxide (TiO_2) and solar UV, possibly combined with hydrogen peroxide (H_2O_2), and homogeneous processes such as Fenton (Fe^{2+}/H_2O_2) and photo-Fenton ($Fe^{2+/}H_2O_2$/UV) reactions have proved to be useful tools for the treatment of pesticide-containing wastewaters. The photo-Fenton process was the most efficient one **(Malato S. et al., 2000)**. A prominent example of AOPs application to the treatment of a real pesticide-contaminated wastewater is the one performed since 2004 at ALBAIDA

Recursos Naturales y Medio Ambiente S.A, in Spain. This company selectively collects empty plastic pesticide containers from greenhouses in El Ejido, Almeria (southeastern Spain) for recycling. The containers are shredded and washed, producing rinse water contaminated with pesticides, with an initial Chemical Oxygen Demand (COD) ranging between 200 and 500 mg L^{-1}. In this effluent, it was also possible to detect and quantify twelve pesticides, with the highest individual concentration of about 1000 g $L^{-1.}$ The treatment strategy adopted uses solar photo-Fenton, performed in a photocatalytic reactor based on solar compound parabolic collectors (CPCs)

Fenton’s reagent (mixture of hydrogen peroxide and ferrous iron) is one of the most effective methods of the oxidation of organic pollutants (**Plant L. et al.,1994**). Fenton’s reaction is based on the catalyzed decomposition of hydrogen peroxide by iron (II) to produce very reactive hydroxyl radicals:

$$Fe_2+ + H_2O_2 \rightarrow Fe_3+ + OH^- + OH^* \quad (1)$$

The hydroxyl radicals which are second only to fluorine among common oxidants, could react rapidly and Non-selectively with nearly all–organic pollutants (**Safarzadeh-amiri A. et al., 1997; Scott j.P. et al., 1995**). Fenton's reagent was found to be very effective in treating various industrial wastewater components, including aromatic and aliphatic compounds (**Tang W.Z. et al., 1996; Koyama O. et al., 1994**) a wide variety of dye (**Lin S.H. et al., 1995**) as well as many other substances, including pesticides (**Lu M.C. et al., 1994; Arnold S.M. et al., 1995**). Fenton's reagent has been applied in the decomposition of atrazine [2- chloro-4-(ethylamino)-6-(isopropylamino)-j-triazine], which is a potential carcinogenic compound relatively resistant to conventional oxidation methods such as ozonation or chlorine dioxide action and of a high persistence in the environment (**Beltran F.J. et al., 1993) .**To lower the cost of azo dye wastewater treatments, research was performed using cheap catalysts for Fenton-like processes, e.g. fly ash and zero valent iron, since they are lowcost adsorbents and catalysts for dye removal from wastewater. (**Dinesh M. et al.,2000**) studied the adsorption mechanisms of removing dyes from wastewater with fly ash and found the sorption capacity of fly ash under investigation was comparable to that of other commercially available adsorbents used for the removal of cationic dyes from wastewater. Most of the ingredients of fly ash are frequently used to catalyze the decomposition of H_2O_2 in peroxidative treatment of various hazardous industrial effluents to less toxic environmentally dischargeable effluents **(Hofmann et al., 1992; Lothar and Walter et al., 1993**). Thus, fly ash seems to be an active heterogeneous catalyst for H_2O_2-based oxidative degradation of hazardous effluents. Fly ash-H_2O_2 system for refractory pollutants degradation have several advantages: fly ash is inexpensive, the deactivation rate is low (even after a number of repeated uses), and separation from the treated effluent is relatively simple. So, fly ash can be used as a catalyst for purifying organic wastewater.

Chapter 2

Pesticide pollution and their advanced treatment techniques

2.1 Overview

Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. A large number of pesticides and herbicides are currently in use worldwide for agricultural and non-agricultural activities for several of benefit (Figure 2.1). These include crop protection, preservation of food and materials and prevention of vector-borne diseases etc. At present, India is the largest producer and consumer of pesticides in Asia and ranks twelfth in the world for the use of pesticides with an annual production of 90,000 tons (**Abhilash P.C., 2008**). A vast majority of the population in India (56.7 percent) is engaged in agriculture and is therefore exposed to the pesticides used in agriculture (**Randhawa G.K., 1999**).

Fig (2.1) Excessive pesticide used in fields (Go Organic, No more GMO's on facebook.com)

The term "pesticide" is a composite term that includes all chemicals that are used to kill or control pests. In agriculture, this includes herbicides (weeds), insecticides (insects), fungicides (fungi), nematocides (nematodes), and rodenticides (vertebrate poisons).(fig 2.2)

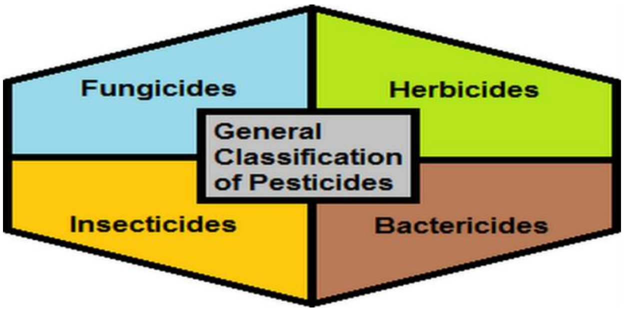


Fig (2.2) Pesticides- Classification by use

Types of pesticides

Insecticides : They are used for killing the insects (eg. Organochlorines, Organophosphates and Carbamates).This category also includes insect repellents such as diethyltoluamide (DEET) and citronella (of natural origin).

Herbicides : Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. They are weedkillers (e.g. Paraquat, Glyphosate and Propanil).

Fungicides : Fungicides are chemical compounds used to prevent the spread of fungi or plants in gardens and crops, which can cause serious damage resulting in loss of yield and thus profit. Fungicides are also used to fight fungal infections (eg. Thiocarbamates, Dithiocarbamates).

Rodenticides : They are use to kill mice, rats, moles and other rodents.Rodenticides are a category of pest control chemicals intended to kill rodents.Rodents are difficult to kill with poisons because their feeding habits reflect their place as scavengers (eg. Warfarines Indanodiones).

Fumigants : They are pesticides that exist as a gas or a vapour at room temperature and may be used as insecticides, fungicides or rodenticides, especially in closed storage places. They are extremely toxic, due to their physical properties, rapid environmental dissemination and human or animal absorption (eg. Cyanide, aluminium phosphate and Methyl bromide).

An herbicide is a substance used to kill unwanted plants. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often synthetic “imitations” of plant hormones. Herbicides used to clear waste ground, industrial sites, railways and railway embankments are non-selective and kill all plant material with which they come into contact.

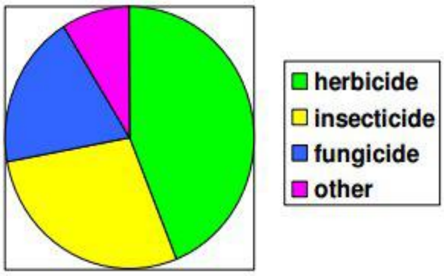


Figure 2.3: Use of pesticides (Global Pesticide Use 2001 (%)

2.2 Human health effects of pesticides

UNEP (1993) linked the effects of pesticides to "the level of oncological (cancer), pulmonary and haematological morbidity, as well as on inborn deformities and immune system deficiencies**".**

Human health effects are caused by:

1. Skin contact: handling of pesticide products
2. Inhalation: breathing of dust or spray
3. Ingestion : pesticides consumed as a contaminant on/in food or in water.

Farm workers have special risks associated with inhalation and skin contact during preparation and application of pesticides to crops. However, for the majority of the population, a principal vector is through ingestion of food that is contaminated by pesticides. Degradation of water quality by pesticide runoff has two principal human health impacts. The first is the consumption of fish and shellfish that are contaminated by pesticides; this can be a particular problem for subsistence fish economies that lie downstream of major agricultural areas. The second is the direct consumption of pesticide-contaminated water. Many health and environmental protection agencies have established "acceptable daily intake" (ADI) values which indicate the maximum allowable daily ingestion over a person's lifetime without appreciable risk to the individual. For example, in a recent paper by (**Wang and Lin.,1995**) studying substituted phenols, tetrachlorohydroquinone, a toxic metabolite of the biocide pentachlorophenol, was found to produce "significant and dose-dependent DNA damage". Traditionally, herbicides in water are removed using granular or powdered activated carbon , nanofiltration , ozonation, and isolation of specific bacterial cultures, but these processes have inherent limitations in applicability, effectiveness, and costs. Advanced Oxidation Processes (AOPs) have been proposed in recent years as an attractive alternative for the treatment of contaminated ground, surface, and wastewater containing pesticides or non-biodegradable organic pollutants. The most commonly used AOPs utilized H_2O_2, O_3 or O_2 as the oxidant. Among AOPs, the combined systems $UV/TiO_2/H_2O_2$ and $UV/Fe^3/H_2O_2$ are considered as the most promising for the remediation of contaminated waters.

2.3 Treatment technologies

It has been demonstrated that Fenton‘s reagent is able to destroy toxic compounds in waste waters such as phenols and herbicides. Production of OH radicals by Fenton reagent occurs by means of addition of H_2O_2 to Fe^{2+} salts.(**Haber F., and Weiss J., 1934**)

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \qquad (1)$$

This is a very simple way of producing OH radicals neither special reactants nor special apparatus being required. This reactant is an attractive oxidative system for waste water treatment due to the fact that iron is very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. The oxidation using Fenton‘s reagent has proven a promising and attractive treatment method for the effective decolonization and degradation of dyes (**Wang A. et al., 2005**). The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants (**Titus M.P. et al., 2004**) . Hydroxyl radicals may react with ferrous ions to form ferric ions or react with organics:

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \qquad (2)$$

$$OH^{\bullet} + \text{organics} \rightarrow \text{products} \qquad (3)$$

Hydroxyl radicals can also react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, which are shown below

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{2\bullet} \qquad (4)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \qquad (5)$$

Ferrous ions and radicals are produced during the reactions. The reactions are shown in Eqs. (6)–(9) (**Titus M.P et al., 2004**)

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \quad (6)$$

$$FeOOH^{2+} \rightarrow HO^{2\bullet} + Fe^{2+} \quad (7)$$

$$HO^{2\bullet} + Fe^{2+} \rightarrow HO^{2-} + Fe^{3+} \quad (8)$$

$$HO^{2\bullet} + Fe^{3+} \rightarrow O2 + Fe^{2+} + H^+ \quad (9)$$

2.4 Fly ash used as a catalyst in Fenton reaction

Fly ash (FA) is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Ash which does not rise is termed bottom ash. In an industrial context, fly ash usually refers to ash produced during combustion of coal. Fly ash is a waste material originating in large quantities from modern power stations. Although, it has been successfully used as a mineral admixture in concrete and brick production, there are still superfluous fly ashes in some countries causing environmental and disposal problem. The utilization of fly ash for removal of pollutants can be rewarding to both environment and economy (**Lin et al., 2008**). Common fly ash disposal practice involves on-site ponding, followed at appropriate intervals, by mining and subsequently land filling the ash material. Less than 10% collected is utilised in some process other than direct burial. The most common processes include the use of fly ash as a raw material in the manufacture of brick and as a pozzolan in concrete . Fly ash has potential use in wastewater treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area. Table (3.1) below shows the engineering properties of Fly Ash.

Table (2.1): Engineering properties of Fly Ash **(Mallik et al., 1997)**

Specific gravity	1.90-2.55
Plasticity	Non Plastic
Proctor compaction – Maximum dry density (gm/cc)	0.90-1.60

Optimum moisture content (%)	38.0-18.0
Angle of internal friction (O)	30^0-40^0
Cohesion (kg/cm 2)	Negligible
Compression index	0.05-0.4
Permeability (CM/SEC)	10^5-10^3
Particle size distribution: Clay size fraction (%)	1-10
Silt size fraction (%)	8-85
Sand size fraction (%)	7-90
Gravel size fraction (%)	0-10
Coefficient of uniformity	3.1-10.7

A relatively small percentage of the materials find application as an ingredient in cement and other construction products, but the vast majority of materials generated each year is held in ash dams or similar dumps. This unproductive use of land and the associated long-term financial burden of maintenance have led to realization that alternative uses for fly ash as a value-added product beyond incorporation in construction materials are needed. Recently, utilization of fly ash in such areas as novel materials, waste management, recovery of metals and agriculture has been explored (**Meunier L. et al., 2006**) . Several techniques have been employed to remove pesticides from wastewater, including adsorption, adsorption chemical oxidation, electrochemical degradation etc. These processes will remove the pollutants but do not degrade them completely. So, different technologies are developed for the elimination of these pollutants completely from water. These chemical procedures are based on the application of oxidizing reagents such as UV radiation, ozone, hydrogen peroxide, etc (**Hoigne J. et al., 1998**) or combination of oxidants in the advanced oxidation processes (AOPs) (**Buxton G.V. et al.,1988**) . These AOPs are characterized by the employment of high oxidation-potential sources to produce the primarily oxidant species hydroxyl radicals, which react with most organic compounds with rate constants in the range 10^7-10^{10} $M^{-1}s^{-1}$. Advanced Oxidation Processes (AOPs) are chemical oxidation techniques able to produce in situ reactive free radicals, mainly the hydroxyl radical ($HO^{\cdot}$), by means of different reacting systems. The concept was originally established by **(Glaze et al., 2000)** as “oxidation processes which generate hydroxyl radical in sufficient quantity to affect water treatment”. Among AOPs, oxidation using Fenton’s reagent is an attractive treatment for the effective degradation of pollutants because of its low cost, the lack of toxicity of the reagents. When FA reacts with hydrogen peroxide, it forms the Fenton-like reaction system, because Fly Ash contains iron component, which can produce ions on dissolving in acid solutions (**Tao C. et al., 2007**) . The photo-Fenton process involves the reaction of ferrous ions (catalyst) and hydrogen peroxide (oxidizing agent) under UV/visible radiation to form active oxidant species, mainly hydroxyl radical, which oxidize organic compounds when they are present in aqueous solution. Compared to other oxidants, hydrogen peroxide is not expensive, not dangerous, easy to handle and poses no lasting environmental threat since it readily decomposes to water and oxygen. Such an easy and economical mode to generate hydroxyl radicals has promoted this oxidation method for wastewater treatment. Another important advantage of the photo-Fenton process is the inexistence of mass transfer limitations due to its homogeneous catalytic nature. Main purpose of our work is to design a solar Fenton system in which fly ash is used as a catalyst in Fenton reaction with H_2O_2 as an oxidant for degradation of waste water.

Objective of present study:

Main objective of the study is to treat technical grade herbicide which cannot be completely treated by conventional treatment technologies. In an attempt to increase the efficiency of degradation of the pesticides present in the wastewater and to improve the economics of the treatment, we use fly ash for treatment of waste water using advanced oxidations processes. This treatment does not transfer pollutants from one phase to another and leads to complete mineralization of organic nonbiodegradable compounds into simpler end products. On the basis of literature reactive Isoproturon was selected, the work was carried out on the degradation of isoproturon using different advanced oxidation processes. Solar photo Fenton, dark Fenton and UV Fenton is compared to check which have the best efficiency to degrade the pesticide

The study is undertaken with the following objectives:-

1. To study the degradation of model pesticide using different Fenton process and fly ash as iron source and compare their efficiencies.

2. Process optimization by varying the parameters like oxidant dose, iron dose, pH, UV intensity, initial concentration of pollutant, temperature variations etc.
3. Reusability studies of the fly ash in context to the degradation of compound.

Chapter 3

REVIEW OF LITERATURE

The work in the present thesis is based on the use of fly ash as an iron source, which constitute the heterogeneous photo-Fenton in the presence of solar energy for the destruction of organic pollutants in aqueous media. Sunlight is captured by the fly ash, which, in the presence of hydrogen peroxide, generates hydroxyl radicals at acidic pH. The latter react with and oxidize organic molecules present in aqueous solution. Fly ash, a solid waste of coal-fired thermal power plants, contains a number of metallic and non metallic oxides like SiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, Mn_2O_3, and TiO_2 and/or their complexes such as quartz, aluminosilicates, ferrite, mullite, hematite, magnetite, and rutile, including some unburned carbon in varying amounts (**Khanra S. et al., 1998**). Fly ash, because of its pozzolanic activity, is used in stabilization/solidification of hazardous solid wastes and sludges (**Ray A. et al., 1992; Parsa J. et al., 1996)**. The sequential utilization of fly ash as a catalyst in peroxidative detoxification of wastewater and as a stabilizer in solid waste modification or as an admixture in mortar/concrete may partly solve its acute disposal problem. Although a considerable number of studies have been reported on the pozzolanic property of fly ash, very little attention has been paid to its catalytic activity (**Dlugi and Gusten 1983; Idriss and Seebauer 1996**). Literature survey shows that some metal ions (e.g. $Cr^{6+,}$ $Mn^{2+,}$ $Cr^{3+,}$ $Fe^{3+,}$ $Cu^{2+,}$ $Ni^{2+,}$ etc.) can combine with H_2O_2 to form Fenton-like reagents and produce hydroxyl. Most of the above metal oxides, metal complexes, and/or unburnt activated carbon are frequently used to catalyze the decomposition of hydrogen peroxide in the course of oxidative purification of various hazardous industrial effluents to less toxic and environmentally dischargeable effluents. Hence, fly ash is also an active and cheap heterogeneous catalyst in H_2O_2-based oxidation of various industrial wastewaters. This report discusses the potential of fly ash as a catalyst in H_2O_2-based degradation of pollutants. Among the treatment technologies for the degradation of pollutants in waters, advanced oxidation processes (AOPs) present a particularly attractive option. In the area of advanced oxidation processes and their applications for the treatment of contaminated waters, the photo-Fenton process has been proven to be an effective treatment for a large number of organic substances like phenols, halogenated compounds, pesticides, antibiotics, dyes, etc

3.1 Fenton and Photo Fenton reaction

The reaction between dissolved iron and H_2O_2 was first described by Fenton in 1894, and the reaction can be described by Equations 3.1 and 3.2 (**Benatti C.T. et al., 2006**): Depending on the solution pH, ferrous and ferric ions can exist in the form of a range of hydrolysis species or other inorganic complexes. For pH 2 – 7 and in the absence of strong inorganic ligands, ferrous ion presents in the form of Fe^{2+}. For the ferric ion, Fe^{3+} exists below pH 3, $FeOH^{2+}$ at about pH 3, and $Fe(OH)^{2+}$ for pH 3–7 (**Wadley and Waite, 2004**) The Fenton process usually involves four stages: pH adjustment, oxidation, neutralisation, and coagulation and precipitation **(Bautista P. et al.,2007)** variously listed the following advantages of using the Fenton process for wastewater treatment:

- The reagents are easy-to-handle, inexpensive, abundant, non-toxic and environmentally benign in diluted form, and they possess oxidative and coagulative properties,
- No additional energy input required to activate H_2O_2, hence a cost effective method to generate OH*,
- No special equipment required, and
- Short reaction time and high efficiency compared with some AOPs.

Usually, ferrous ion (Fe^{2+}) was used as the source of iron and its superiority over ferric ion (Fe^{3+}) has been demonstrated by (**Wang S., 2008**) in the treatment of azo dye wastewater by the Fenton process. The effects of Fe^{2+} or Fe^{3+} dosage, H2O2 concentration, pH, and temperature were investigated and reported the following findings: Higher rate of dye degradation was observed when Fe^{2+} was used instead of Fe^{3+} although a similar extent of degradation was achieved (95% of about 0.07 mM dye was removed), Increased iron dosages and H_2O_2 concentration accelerated the rate of dye degradation, Decrease in pH from 6.3 to 2.4 or 3.4 significantly improved the degradation rate, and degradation rate deteriorated at temperature higher than $45^{o}C$.

The literature related to the Fenton process was reviewed by (**Gogate and Pandit., 2004**) and the important operational parameters were identified as Fe^{2+} and H_2O_2 dosages, initial concentration of pollutants, pH, and type of buffer used for pH adjustment. The degradation rate of pollutants was accelerated with increased Fe^{2+} concentration. However, excessive Fe^{2+} dosage only increased the degradation rate marginally and contributed to increased total dissolved solids. The need to remove residual dissolved iron and the problem related to sludge disposal have been pointed out by (**Bautista P. et al., 2007).** The optimum pH condition was found to be 3–4, and the highest oxidation efficiency was reported when acetic acid/acetate buffer was used instead of phosphate and sulphate buffers which encouraged the formation of stable Fe^{3+} complexes. Problems such as corrosion of equipment (due to the acidic conditions) and inability to break down refractory chemicals (e.g., acetic acid, acetone, carbon tetrachloride, methylene chloride, *n*-paraffins, maleic acid, malonic acid, oxalic acid, and trichloroethane) were discussed. The Fenton process has been used by **(Benatti C.T. et al.,2006**) to treat chemical laboratory wastewater, and the COD removal was maximised by using response-surface optimization techniques in which H_2O_2:COD, Fe^{2+}:H_2O_2, and pH were used as the control factors. The required amount of H_2O_2 was added in three equal portions at intervals of 20 minutes. The oxidation stage was maintained at pH 4 for 4 hours before adjustment to 8 and subsequent settling for 15 hours. Although many reports suggested that up to 30 minutes was sufficient for the reaction to reach equilibrium **(Gulkaya I. et al.,**

2006; Tekin H. et al., 2006), the reaction time of 4 hours for the oxidation might not be excessive since others have also reported a longer oxidation time . On the other hand, long settling times for the Fenton process have also been observed by (**Neyens and Baeyens.,2003**) and they recommended the use of a flocculant aid such as a polymer. Fenton reaction rates are strongly increased by irradiation with UV/visible light **(Arslan I. and Balcioglu I.A., 2011)**. During the reaction, Fe^{3+} ions are accumulated in the system and after Fe^{2+} ions are consumed, the reaction practically stops. Photochemical regeneration of ferrous ions (Fe^{2+}) by photo reduction of ferric ions (Fe^{3+}) is the proposed mechanism. The new generated ferrous ion reacts with H_2O_2 generating a second OH* radical and ferric ion, and the cycle continues.

In the presence of light

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + OH^{*}$$

Fenton and photo-Fenton reaction depend not only on H_2O_2 concentration and iron added, but also on the operating pH value. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water. **(Barbusiński K. et al., 2000)** analyzed the process of pesticide removal from waste water using Fenton reaction. It was found that most of the pesticides were completely degraded at H_2O_2 concentration of 2.5 g/dm^3 . The optimum ratio of $[Fe^{2+}]$ to $[H_2O_2]$ was from 1:3 to 1:2 while the optimum pH was from 3.0 to 3.5. It was a most effective process for fenitrothion and chlorfenvinphos which were degraded from 97 to 100% whereas organochlorine pesticides were removed with efficiency of more than 90%. (**Joonseon Jeong and Jeyong Yoon, 2005**) found that pH is one of the most important factors in Fenton based reactions. They found out that pH is one of the critical operating parameters, due to the fact that the Fenton reaction can work only under acidic pH conditions. It is hoped that Ferric iron complexed with oxalate (Fe(III)-oxalate; ferrioxalate) will provide an alternative to the traditional Fenton process with, its limited range of pH conditions, since its high solubility in aqueous media can broaden the available pH range of the Fenton reaction up to the near neutral pH regime. The Fenton process (Fe^{2+}/H_2O_2), one of the AOPs, is widely used as a suitable treatment method for highly concentrated wastewater, due to its effectiveness in producing OH* (**Barbeni M. et al., 1987; Kang S. et al., 2002)**There are many different ways to produce HO^-, among which the photo-Fenton process has shown to be the most efficient one for pesticide-containing wastewater treatment **(Oller I. et al., 2006; Maldonado M.I. et al., 2007)**, achieving higher reaction yields with lower treatment costs, mainly due to a more efficient use of solar light as photon source **(Malato S. et al., 2004).** The photo Fenton system involves the reaction of ferrous ions, Fe^{2+}, and hydrogen peroxide, H^2O^2, to form the active HO^- (Fenton process) and, under UV-Vis radiation, Fe^{3+} can be reduced to Fe^{2+} closing a loop mechanism where iron species act as catalyst, giving rise to additional HO^- (photo-Fenton process**)** **(Pignatello J.J., 1992).**

(Yap C.L et al.,2010) reviewed the applications of Fenton based treatments specifically for polycyclic aromatic hydrocarbons-contaminated soils. They overviewed of the background and principles of Fenton treatment catalysed by both homogenous (conventional and modified Fenton) and heterogeneous (Fenton-like) catalysts are firstly presented. Laboratory and field soil remediation studies are then discussed in terms of efficiency, kinetics and associated factors. Four main scopes of integrated Fenton treatments, i.e. physical- Fenton, biological-Fenton, electro-Fenton and photo-Fenton are also reviewed. For each of these integrated remediation technologies, the theoretical background and mechanisms are detailed alongside with achievable removal efficiencies for polycyclic aromatic hydrocarbons in contaminated soils compared to sole Fenton treatment. Finally, the environmental impacts of Fenton based soil treatments was discussed. An efficient combined treatment for the decontamination of a pesticide containing wastewater resulting from phytopharmaceutical plastic containers washing, presenting a moderate organic load (COD = 1662-1960 mg O_2 L^{-1}; DOC = 513-696 mg c L^{-1}), with a high biodegradable organic carbon fraction (81%; BOD^5 ¼ 1350-1600 mg O_2 L^{-1}) and a remaining recalcitrant organic carbon mainly due to pesticides was proposed by (Vitor J.P. et al in 2012). Nineteen pesticides were quantified by LC-MS/MS at concentrations between 0.02 and 45 mg L^{-1} (14-19% of DOC). Mineralization of solutions containing a mixture of three phenolic compounds, gallic, p-coumaric and protocatechuic acids, in a ferrioxalate-induced solar photo-Fenton process was studied by **(Monteagudo J.M. et al., 2010)**. coumaric and protocatechuic acids, in a ferrioxalate-induced solar photo-Fenton process was investigated. The reactions were carried out in a pilot plant consisting of a compound parabolic collector (CPC) solar reactor. An optimization study was performed combining a multivariate experimental design and neuronal networks that included the following variables: pH, temperature, solar power, air flow and initial concentrations of H_2O_2, Fe (II) and oxalic acid. Under optimal conditions, total elimination of the original compounds and 94% TOC removal of the mixture were achieved in 5 and 194 min, respectively. pH and initial concentrations of H_2O_2 and Fe(II) were the most significant factors affecting the mixture mineralization

3.2 Properties of fly ash

(**Wei X. et al., 2012**) studied of the physico chemical properties of fly ash from two kinds of coal-fired power plants .Three aspects were examined: the micro-morphology, the mineral composition and the content of heavy metals. The results show that the fly ash from plants using a circulating fluidized bed are more irregular particles, while the particles from the plants using a pulverized coal-fired boiler are mainly spherical in shape. Quartz and mullite are the main crystalline phases in the ash. Clearly, both the technology and the coal used by a power plant can influence the mineral composition of the ash. The mineral composition of fly ash from a circulating fluidized bed is more complex than that from a pulverized coal-fired boiler. The quantity of elements found in the fly ash is greater than that found in the bottom ash for the same plant. Heavy metals are likely to be enriched in the fly ash. Heavy metal leachability was studied using two leaching methods. The results indicate that most of the heavy metals that leached during either batch leaching or column leaching experiments did not exceed the related maximum concentration standards. But Ni concentrations in the leachates from both batch and column tests exceed the standard. The highest excess rates in both tests were 572% and 497%, which levels might threaten the environment.

(**Cetin S. et al., 2007**) studied fly ash and activated carbon for their ability to remove nickel [Ni(II)] and zinc [Zn(II)] from an aqueous solution. The effects of contact time, pH, initial metal concentration and amount of adsorbent on the adsorption process at 20±2 ◦C were studied. Batch kinetic studies showed that an equilibrium time of 1 h was required for the adsorption of Ni(II) and Zn(II) on both adsorbents. The maximum metal removal was found to be dependent on solution pH (4.0 for Ni (II) and Zn (II)). With an increase in the concentrations of these metals, the adsorption of Ni (II) and Zn (II) decreased on both of the adsorbents. The effectiveness of fly ash as an adsorbent improved with increasing calcium (CaO) content. Adsorption data in the range of pH values (3.0–8.0) using Ni(II) concentration of 25±2 mg/L and Zn(II) concentration of 30±2 mg/L in solution were correlated using the linear forms of the Langmuir and Freundlich equations. The fly ash was found to be a metal adsorbent as effective as activated carbon.

(**Blanco F. et al., 2005**) studied that coal-burning power plants that consume pulverized solid fuels produce large amounts of fly ash as a residue. Fly ashes have been used in construction, agriculture, metal recovery and water pollution control. This paper considers the variation in properties of fly ashes to be used in the field of construction. The fly ashes produced in two coal-burning power plants in Asturias (Spain) were physically and chemically characterized in order to determine their pozzolanic activity and reactivity. Fly ashes are used as hydraulically active additives as they are a finely divided inorganic material; they were examined to determine whether they could be used as special preservatives in cements and concretes. To improve their properties, they are mechanically activated by wet milling as well as chemically activated by leaching with 30% by weight sulfuric acid at different temperatures and times.

Fly ash is the powdery residue obtained by the separation of the solids from the flue gases of furnace fired with the pulverized coal., It is also known as a complex heterogeneous material and as the finest coal combustion residue (0.2-90μm) formed during the transformation of mineral matter present in coal particles after combustion. More so, poor combustor efficiency and the improper quality control in maintaining the particle size of the pulverized coal feed into the combustors can also leads to a wide distribution of char, semi coke or coked carbon of large dimension (90-300μm) in the ash generated. These particles are collected using a variety of methods such as mechanical collectors, electrostatic precipitators, fabric filters and wet scrubbers (**Lee Daniels W. et al., 2006**).

The detailed chemical characteristics of fly ash can be explained based on its mineralogical composition which depends largely on its geological features related to formation, origin of coal, decomposition of coal and combustion condition .The mineralogy of fly ash is closely related to the minerals entrained in the coal and several different minerals have been identified as part of fly ash. The major phase's presents in the fly ash are mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anhydrite ($CaSO_4$), hematite (Fe_2O_3), lime (CaO) and an amorphous aluminosilicate. However, the formation of these phases depends on the type of coal used during combustion. In addition, the mineral contents of the FA are found responsible for its applications as fillers in polymer, refractory materials, as soil ameliorant and as an adsorbent for inorganic removal from wastewaters .The chemical composition of fly ash is determined from the source of coal used during combustion, Combustion conditions and variation in composition with particle size .The major elements in fly ash are Si, Al and Fe with smaller concentration of S, Ca and Mg and with oxygen as the main constituent in the form of various minerals. Trace elements present in the ash includes Pb, Zn, Cr, Ag, As, Cd, Ni and other minor metals (**Goodarzi F., 2005**).

3.3 Coarse / fine fly ash

Two cement producers in Heidelberg Cement North Europe, have long experience with intergrounding of fly ash and clinker to produce cement. Both have found improved properties. The fly ash cement (Norcem Standard fly ash CEM II A/V) is produced by adding fly ash to the mill inlet or to the mill separator. In both cases the coarse particles will be separated back into the mill until they are fine enough. This gives a finer and more reactive fly ash than the fly ash added directly into the concrete mixer.(**Norcem and Lehigh 2004**)

(**Jaturapitakkul C. et al.,2000**) investigated the strength activity index of ground coarse fly ash and fine fly ash. Four different fly ashes replaced cement 20 % by weight to make mortars. They find out that strength activity index of coarse fly ash can be improved by grinding. The chemical composition did not change much of the different particle size. For a good quality of fly ash, either by classifying or grinding, the important factor is fineness, but also shape of the particles. Fly ash with small particle size increased strength and the strength gain. They also experienced that to keep the same workability of mortar, the fine fly ash demanded less water than the coarse one.

(**Chindaprasirt P. et al., 2001**) Studied the effect of fly ash fineness on the compressive strength of concrete. Three fly ash finenesses (100 % original coarse fly ash, medium fine with 45 % of original fly ash, fine with 10 % of the original fly ash), fly ash dosage of 30 % of binder in three concrete mixes, low, medium and high strength concrete, the strength was measured up to 90 days. They find out that the strength of fly ash concrete were higher than those of the Portland cement concrete in the same group. The reduction of the water content, the good dispersing and filling effect of the fly ash contribute to the good strength development of the fly ash concrete. With use of finer fly ash, the water content was further reduced and strength of concrete enhanced further. He has also investigated the influence of fly ash fineness on strength, drying shrinkage and sulphate resistance of blended cement mortars. In addition to original fly ash, five different fineness values of fly ash were obtained by sieving and using an air separator. They found out that fine fly ash gave increased strength because of the packing effect and reduced water demand. The coarse fly ash, lacking both the medium and fine fraction, increased the water demand owing to the rougher surface of the coarser particles. The drying shrinkage was reduced for all of the mortars with fly ash. The fine fly ash has reduced expansion of the mortar bars immersed in the sodium sulphate solution.

(**Erdogdu K. and Tűrker , 2000**) found that sieved fine fly ash increased the strength of mortar samples compared to that of the mortar made from the original coarser fly ash. They also found out that the chemical composition did not vary from the fine to the coarse fraction of the investigated Class F fly ash. Two fly ashes were tested, one coarse and one finer. Two cements were also tested, a commercially available ASTM type III cement and a laboratory made normal Portland cement. Blaine of the fly ash was respectively 196 and 306 m^2/ kg. The blended cement had a blaine of about 550 m^2/kg. The coarse fly ash that fails to meet the fineness requirements of ASTM C618 had been used successfully to produce high volume fly ash blended cement. The mechanical and durability properties of concrete made with this blended cement, was comparable with the finer fly ash blended cement. The production of blended cements offers a possible way for the utilization of coarse fly ashes

3.4 Fly ash for waste water treatment

(**Li J.T. et al., 2010**) studied an efficient and convenient method for degradation of Acid orange 3 (AO_3) dye from aqueous solution by combination of Fly ash/H_2O_2 and ultrasound irradiation. The effects of the relevant operating conditions (pH value, dye concentration, H_2O_2 concentration, dosage of Fly ash and different reaction system) on the degradation of (AO_3) were also observed. The combination method was found to be effective and could yield better results than either sonolysis or Fenton-like oxidation individually. Removal of 96% was obtained under the optimum conditions (dye concentration, 100 mg/L; H_2O_2, 5.4 mM; Fly ash, 2.5 g/L; pH 3, ultrasonic irradiation frequency of 25 kHz, room temperature).

(**Song Y.L. et al., 2009**) investigated the degradation of C.I. Direct Black 168 from aqueous solution using Fenton-like reactions combining ultrasound. In the presence of H_2O_2, the effect of the heterogeneous catalysts, such as fly ash, kaolinite or diatomaceous earth on the degradation of Direct Black 168 was observed under ultrasound. The fly ash was the most efficient catalyst. It is apparent that ultrasound can prompt the reaction to take place and give in higher degradation. In the combination of ultrasound and fly ash/H_2O_2, the effect of different system variables namely concentration of the dye, dosage of fly ash, concentration of H_2O_2, pH of solution and the addition of NaCl were studied. 99.0% removal ratio was achieved at initial concentration 100 mg/L, pH 3.0, and dosage of fly ash 2.0 g/L, as well as 2.94 mM H_2O_2. NaCl exhibited only a minor effect on the dye removal.,

(Liu Z. et al., 2000). Explored the potential use of fly ash from coal as a heterogeneous catalyst in the degradation of azo dye by using H_2O_2 irradiated by microwave. The effects of various parameters such as fly ash loading, temperature, pH, initial concentration of methyl orange, and dosage of H_2O_2, and deactivation of catalytic effect of fly ash were studied. The metal oxide compounds in fly ash, such as iron and manganese, can combine with H_2O_2 to form a Fenton-like reagent and produce hydroxyl radical, which can oxidize persistent organic pollutants into small molecule compounds. Under microwave irradiation, methyl orange (MO) solution, a typical azo dyestuff selected as a model pollutant, was decolorized. For the 100mL 1000mg/L MO solution, the decolourization and COD removal ratios were 99.8% and 80%, respectively, with a pH of 2, 2 grams of fly ash, 1 mL of 30% H_2O_2, 800 W of microwave power, and an irradiation time of 5 minutes. The negligible homogeneous catalytic action of trace metals leached from the fly ash such as Fe, Mn, and Cu, confirmed the sole heterogeneous catalytic nature of fly ash particles in the cleavage of azo bonds. Fly ash deactivation was found to be <40% in 4 repeated uses.

(Raymond-Ooi E.H. et al., 2004) investigate the influences of several factors on the desulfurization capacity of absorbent prepared from coal fly ash, CaO, and $CaSO_4$. The absorbent was synthesized using hydrothermal reaction while the sulfation experiments were performed in a fixed-bed reactor under isothermal conditions at low temperature. Specifically, the effects of reaction temperature ($60 < T < 80$ºC), SO_2 inlet concentration ($500 < Co < 2000$ mg/l), relative humidity ($50 < RH < 70\%$) and absorbent particle size ($200 \leq PS \leq 600$ μm) on the desulfurization capacity of the absorbent were investigated. In general, the desulfurization capacity of the absorbent was found to increase with higher relative humidity but with decreasing SO_2 inlet concentration and absorbent particle size. The reaction temperature was found to have negligible effect on the desulfurization activity. The chemical composition of the absorbent before and after SO_2 capture was characterized using X-ray diffraction (XRD). The diffraction spectrum showed that calcium aluminium silicate hydrate and calcium carbonate were formed during the hydration process. However, after reacting with sulphur dioxide, aluminium silicate hydrate and calcium sulphate were the prominent phases detected in the spent absorbent.

(**Lin J.X. et al., 2008**) studied the low-cost adsorbent for the removal of a typical dye, methylene blue, from aqueous solution. An increase in the specific surface area and dye-adsorption capacity was observed after the acid treatment. The adsorption isotherm and kinetics of the treated fly ash were studied. The experimental results were fitted using Langmuir and Freundlich isotherms. It shows that the Freundlich isotherm is better in describing the adsorption process. Two kinetic models, pseudo-first order and pseudo second order, were employed to analyze the kinetic data. It was found that the pseudo-second-order model is the better choice to describe the adsorption behaviour.

(**Oluwaseyi S. et al., 2003**) studied the adsorption isotherms and the calculated adsorption capacities show that the SACFA possesses the ability to remove the test adsorbents from water. The adsorption capacity for the adsorbents based on Freundlich constants were found to be 4-Nitrophenol > phenol > 2-Nitrophenol. That is, CFA had the highest adsorption capacity for 4-Nitrophenol within the concentration range studied. This work also shows that contact time of 360 minutes is sufficient for equilibrium to be established between the adsorbents and the adsorbent, but equilibrium time depends on the type of adsorbents and adsorbent used. The contact time of the adsorbents onto CFA are also comparable to the result from (Rengaraj et al., 2002) who reported that a contact time of 2 hours was used on the adsorption of phenol onto palm seed activated carbon. An equilibrium time of 22 hr was used in this study to obtained experimental data used in evaluating the adsorption capacity of the CFA

(**Potgieter J.H. et al., 2009**) studied the rate of adsorption follows first-order kinetics before attaining equilibrium with the sorption rate obtained being the highest for 4-nitrophenol (p-nitrophenol) (7.0 x 103/h), followed by phenol (1.2 x 103/h) and 2-nitrophenol (o-nitrophenol) (1.0 x 103/h). Batch studies were performed to evaluate the adsorption process, and it was found that the Freundlich isotherm effectively fits the experimental data for the adsorbents better than the Langmuir model, with the fly ash having the highest adsorption capacity of 6.51 X 10-2 mg/g for 4-nitrophenol, 6.00 x 10-2 mg/g for 2-nitrophenol and 6.31 x10-2 mg/g for phenol. The fly ash was found to adsorb 90.2% of phenol, 88.9% of 2-nitrophenol and 92.6% of 4-nitrophenol at an initial concentration of 20 mg/ℓ. The desorption studies suggested that the desorption of 4-nitrophenol was the most difficult of the three adsorbents to be desorbed. The desorption efficiency was 17.9% for phenol, 18.8% for 2-nitrophenol and 10.2% for 4-

nitrophenol. This work proved that SACFA can be used as an efficient adsorbent material for removal of phenol from water and wastewater.

(Moutsatsou A. et al., 2000) investigate lignite fly ash as absorbent material for oil spill in wet and dry environment. The fine particle size, floatability, porosity and specifically the chemical and mineralogical structure of FAs constitute a significant factor for such application. The experiments that took place include the treatment of two types of FA with heating oil, light cycle oil and Iranian light crude oil, so as to simulate all the cases of oil transportations. Parameters studied concerned the rate of mixing, the time and type of stirring and the quantity of water and oil absorbed. The results showed that the absorbance efficiency was influenced by the viscosity of the oil. Table 2 would help us to know the chemical composition of Fly Ash.

Table3.1: Chemical composition of fly ashes.

%(w/w)	FA AD	FA M
SiO_2	29.73	51.26
Al_2O_3	13.90	19.39
Fe_2O_3	6.49	8.44
CaO	34.13	11.82
MgO	3.56	2.27
SO_3	5.13	2.91
Na_2O	1.12	0.53
K_2O	0.68	1.81
L.O.I. (loss of ignition)	4.03	1.67

(**Digze N. et al., 2008**) studied adsorption kinetic and equilibrium studies of three reactive dyes namely, Remazol Brillant Blue (RB), Remazol Red 133 (RR) and Rifacion Yellow HED (RY) from aqueous solutions at various initial dye concentration (100–500 mg/l), pH (2–8), particle size (45–112.5 μm) and temperature (293–323 K) on fly ash (FA) were studied in a batch mode operation. The adsorbent was characterized with using several methods such as SEM, XRD and FTIR. Adsorption of RB reactive dye was found to be pH dependent but both RR and RY reactive dyes were not. The result showed that the amount adsorbed of the reactive dyes increased with increasing initial dye concentration and contact time. Batch kinetic data from experimental investigations on the removal of reactive dyes from aqueous solutions using FA have been well described by external mass transfer and intraparticle diffusion models. It was found that external mass transfer and intra particle diffusion had rate limiting affects on the removal process. This was attributed to the relatively simple macropore structure of FA particles. The adsorption data fitted well with Langmuir and Freundlich isotherm models. The optimum conditions for removal of the reactive dyes were 100 mg/l initial dye concentration, 0.6 g/100 ml adsorbent dose, temperature of 293 K, 45 μm particle size, pH 6 and agitation speed of 250 rpm, respectively. The values of Langmuir and Freundlich constants were found to increase with increasing temperature in the range 135–180 and 15–34 mg/g for RB, 47–86 and 1.9–3.7 mg/g for RR and 37–61 and 3.0–3.6 mg/g for RY reactive dyes, respectively. Different thermodynamic parameters viz., changes in standard free energy, enthalpy and entropy were evaluated and it was found that the reaction was spontaneous and endothermic in nature.

(**Wang et al., 2006**) discuss that fly ash is a low cost absorbent. Fly ash is a waste substance from thermal power plants, steel mills, etc. that is found in abundance in the world. In recent years, utilization of fly ash has gained much attention in public and industry, which will help reduce the environmental burden and enhance economic benefit. In this paper, the technical feasibility of utilization of fly ash as a low-cost adsorbent for various adsorption processes for removal of pollutants in air and water systems has been reviewed. Instead of using commercial activated carbon or zeolites, a lot of researches have been conducted using fly ash for adsorption of NO_x, SO_x, organic compounds, and mercury in air, and cations, anions, dyes and other organic matters in waters. It is recognized that fly ash is a promising adsorbent for removal of various pollutants. Chemical treatment of fly ash will make conversion of fly ash into a more efficient adsorbent for gas and water cleaning.

(**Chang S.H. et al., 2009**) investigated the removal of a basic dye, Rhodamine B (RhB), by fly ash adsorption, Fenton oxidation, and combined Fenton oxidation-fly ash adsorption. Even though fly ash is a low cost absorbent, a high dose of fly ash was needed to remove RhB. Only 54% of RhB was removed by 80 g L−1 fly ash. Solution pH did not significantly affect the RhB sorption by fly ash after 8 h. Fenton reagents at H_2O_2 dose of 6×10−3M and pH 3 rapidly decolorized 97% of RhB within 2 min, and 72% of COD removal was obtained at 30 min reaction time. Spectrum analysis result showed that a large area of UV spectrum at 200–400nm remained after Fenton reaction. The addition of 1 g L^{-1} fly ash effectively removed COD from Fenton-treated solution, and the UV absorption spectrum at 220–400nm totally vanished within 2 h. COD removal of RhB by the combined Fenton oxidation and fly ash sorption process was 98%. The COD removal capacity of fly ash for Fenton-treated RhB solution was 41.6 times higher than that for untreated RhB solution. The results indicated that the combined process is a potential technique for RhB removal properties of fly ash.

Biomass fly ash was treated with alkaline solution to enhance its adsorption capacity of Reactive Black 5 dye. The results revealed that the alkaline concentration, solution to fly ash ratio, treatment temperature and treatment time had a positive effect on the dye adsorption capacity of the treated fly ash (TFA), due to dissolving SiO2 and increasing the proportion of unburned carbon. In addition, the dye adsorption behaviour of the TFA in aqueous solution was investigated. The effects of various experimental parameters (initial pH, initial dye concentration and contact time) were determined spectrophotometrically. The dye adsorption capacity of the TFA was maximized at an alkaline pH (8.2–10.4). The adsorption capacity of dye by the TFA increased with increasing initial dye concentration. Equilibrium data fitted well with the Langmuir model in the range of 50–700 mg L^{-1} and the maximum dye adsorption capacity was 107.53 mg g^{-1}. The sorption data provided a good fit with a pseudo-second order kinetic model. These results suggested that treating biomass fly ash with alkaline solution is an effective method for enhancing dye removal efficiency (**Pengthamkeerati P. et al., 2010**)

(Swades K. Chaudhuri and Babita Sur., 2000) studied the potential of coal fly ash as a heterogeneous catalyst in peroxidative decolourization of aqueous solution of several reactive dyes using hydrogen peroxide (H_2O_2). The effects of various parameters (source of fly ash, fly ash loading, temperature, pH, initial concentration of dye and hydrogen peroxide, and deactivation of catalytic effect of fly ash) were studied. The rate of decolourization is zero order with respect to concentration of dye in the range of 50–200 mg/L and first order with respect to concentration of H_2O_2 in the range of 375–2,500 mg/L. It was found that at 333 K and pH 2.0, only 2% (weight/ volume) fly ash loading can completely decolorize 100 mg/L dye solution within 180–1,770 s for an initial H_2O_2 conc of 1,500 mg/L, depending on the source of fly ash and dye used. But maximum 25% decolourization was noticed after 3 h duration of reaction without fly ash. The negligible homogeneous catalytic action of trace amount of metals like Fe, Mn, and Cu leached from the fly matrix confirmed the sole heterogeneous catalytic nature of fly ash particles in decolourization reactions. The deactivation of fly ash was found to be <30% in nine repeated uses. They also studied adsorption dynamics and mechanism of dyes onto fly ash in the absence of H_2O_2.

(**Sarkar A. *et al.*, 2006**) analyse the particle size, specific surface area determination, density and porosity of fly ash are some of the factors that influence the reactivity of fly ash for adsorption processes. Ashes obtained through electrostatic precipitators are finer, while ash collected through mechanical means are coarser. The surface area analysis is one of the factors used to determine the adsorption capacity of any adsorbent, and has been found to increase with the decrease in the particle size of the fly ash. The ash obtained from the burning of bituminous coal is found to be finer than that produced by the burning of lignite coal., This was also observed that the higher sum total of (SiO_2, $Al_6Si_2O_{13}$ and Fe_3O_4) for bituminous coal, its silica content which apparently increases with decrease particle size, low carbon content and the melting of the higher aluminous siliceous material present in bituminous coal are responsible for the generation of ashes with finer particles than that of non bituminous coal.,

3.5 Pesticides

(**Magdalena B.M. et al.,2005**) studied Isoproturon degradation and mineralization in water by four Advanced Oxidation Processes (AOP): UV/H_2O_2, UV/H_2O_2/Fe(II) (photo-Fenton), UV/TiO_2, and UV/H_2O_2/TiO_2 (anatase). All the degradation experiments have been done in a quartz glass photoreactor (V= 0.5 L) equipped with a UV lamp having an incident photonic flux of 5x10-6 Es/s. The initial concentration of the Isoproturon aqueous solution was $5x10^{-5}$ mol/L. The concentrations of the unreacted substrate and of some intermediates have been determined by HPLC analysis**.** The Total Organic Carbon (TOC) measurements have been performed with a TOC analyzer Shimadzu model TOC 5000A. The optimal parameters have been identified for each process. The main conclusion from the obtained results is that the most effective is the photo - Fenton process. Using doses of 0.5 mmol/L H_2O_2 and 0.05 mmol/L Fe (II) the Isoproturon is almost completely removed after only 15 minutes, while TOC is reduced by 88.78 % after 60 minutes of irradiation.

(**Parra S. et al., 2000)** conducted experiments on physicochemical pre-treatment for the destruction of two non-biodegradable herbicides (metobromuron and isoproturon). By different advanced oxidation processes, i.e. the systems UV/TiO_2, UV/TiO_2/H_2O_2, Fe_3C/H_2O_2 and UV/Fe_3/H_2O_2. The degradation rates were always higher for the photo-Fenton reactions when compared with the heterogeneous photocatalytic systems. Optimal concentrations of Fe_3C and H_2O_2 for the abatement of both herbicides in the photo-Fenton system were found . A combined photo-Fenton and biological flow reactor for the degradation of isoproturon was operated in continuous mode at laboratory scale. In this coupled system, 100% of the initial concentration of isoproturon and 95% of TOC were removed. Some field experiments under direct sunlight were carried out at the Plataforma Solar de Almeria in Spain. The obtained results demonstrated that the solar catalytic treatment is effective for the purification of water contaminated by the herbicides under study.

(**Phanikrishna M.V.et al., 2008**) studied photocatalytic degradation of isoproturon under solar light in aqueous suspensions. They investigated immobilization of TiO_2 using a simple solid state dispersion technique over mesoporous Al-MCM-41 support for the treatment of isoproturon herbicide. The parameters like TiO_2 loading over Al-MCM-41, amount of catalyst, concentration of substrate, pH effect, durability of the catalyst, activity comparison of TiO_2 and Al-MCM-41 supported system are studied. The mineralization of isoproturon is monitored by TOC. Based on the degradation products detected through LC–MS, a plausible degradation mechanism is proposed. The data indicates that TiO_2/Al-MCM-41 composite system is an effective photocatalyst for treatment of isoproturon in contaminated water

(**Benitez F.J. et al.,2009**) studied chemical degradation of four phenylurea herbicides (isoproturon, chlortoluron, diuron and linuron) by using UV radiation, ozone and some advanced oxidation processes (UV/H_2O_2, O_3/H_2O_2, Fenton reagent and the photo- Fenton system). The waters used were: ultra-pure water, a commercial mineral water, a groundwater and surface water taken from a reservoir. Elimination levels were established for each herbicide and for several global quality parameters, and a kinetic study was performed in order to determine basic kinetic parameters of each reaction between the target phenylureas and these oxidizing systems.

(**Cox L. et al.,1996**) studied degradation of isoproturon in soil. The herbicide isoproturon was degraded rapidly in a sandy loam soil under laboratory conditions (incubation temperature, **15°C;** soil moisture potential -33 kPa). Degradation was inhibited following treatment of the soil with the antibiotic chloramphenicol, but unaffected by treatment with cycloheximide, thus indicating an involvement of soil bacteria. (Sarah J. Welch)Rapid degradation was not observed with other phenylurea herbicides, such as diuron, linuron, monuron or metoxuron incubated in the same soil under the same experimental conditions. Three successive applications of isoproturon to ten soils differing in their physicochemical properties and previous cropping history induced rapid degradation of the herbicide in most of them under laboratory conditions.

(**Lapertot M. et al.,2007**) studied degradation of mixed pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon) employing photo- Fenton as a preliminary step before biotreatment. Photo-Fenton degradation is an important sub-process in the integrated photobiological process for removal of biorecalcitrant chemicals. Shortening the photo-Fenton treatment time has a critical impact on the economical feasibility of the integrated process. In this study, photo-Fenton was proved to enhance biotraitability of a mixture of biorecalcitrant substances (pesticides). During the photocatalytic process, dissolved organic carbon (DOC) measurements, liquid and ionic chromatography analyses, acute toxicity evaluation using MicrotoxTM and the Zahn–Wellens biodegradability testing were provided to characterize the photo-treated solutions. In order to find out the best moment for coupling of photocatalytic and biological processes, different times of photo-Fenton pretreatment were tested for biotreatment

3.6 Immobilized fly ash

(**Yingjia Z. et al.,2009**) studied immobilized fly ash is an efficient heterogeneous photofenton oxidation catalyst for degradation of phenol**.** Heterogeneous catalyst has been prepared with fly ash loaded with Fe3+,and its effect on the degradation of phenol in UV/Fenton has been studied. The effects of the preparation method on its catalyzing efficiency and stability , the effects of its reaction system, loading capacity of Fe3+,dose of H2O2,and initial pH on phenol degradation efficiency are investigated. Moreover, the reusability of the catalyst is examined**.** The experimental results show that catalyst Fe-A1 prepared by impregnation method has better stability and catalyzing capacity.The standard conditions are as follows:pH=3, H_2O_2 dosage=5.0 mmol/L,and the catalyst dosage=0.2 g/L,the degradation efficiency of phenol reaches above 95% within 60 min for 500 mL of phenol simulated wastewater with an initial mass concentration of 100 mg/L. After the catalyst is reused for 3 times, the phenol degradation efficiency is still above 93% within 60 min

(**Zhanq A. et al., 2012**) removal of p-nitrophenol in water using acid-activated fly ash. The physicochemical characteristics of AFA were better than those of raw fly ash (RFA). Under experimental conditions of pH 1.5-5.1, H_2O_2 dosage 83.3-333 mgL^{-1}, AFA loaded 5.0-20 gL^{-1}, and temperature 298-348 K, the p-NP removal rate increased with the increase of H_2O_2 dosage, AFA loaded and temperature. The highest removal rate (98%) was observed at pH 2.0 when H_2O_2 dosage 166.5 mgL^{-1}, AFA loaded 10 gL^{-1} and temperature 298 K.

(**Visa M. et al.,2013**) studied removal of Methyl-orange and cadmium simultaneous using fly ash and photo-Fenton systems. Wastewaters resulting from the textile and dye finishing industries need complex treatment for efficient removal of colour and other compounds existent in the dyeing and rising baths (heavy metals, surfactants, equalizers, etc.). Modified fly ash (FA) mixed with TiO_2 photo catalyst represent a viable option for simultaneous removal of dyes and heavy metals, and the optimized conditions are discussed in this paper for synthetic wastewaters containing methyl-orange (MO) and cadmium. For a cost-effective dye removal process, further tests were done, replacing the photo catalyst with a Photofenton system. The optimized technological parameters (contact time, amount of fly ash and amount of Fe^{2+} and H_2O_2 allow to reach removal efficiencies up to 88% for the heavy metal and up to

70% for the dye. The adsorption mechanisms and the process kinetic are discussed, also considering the possibility of in situ generation of the Fenton system, due to the fly ash composition.

Chapter 4

Materials and method

Raw sample of technical grade herbicide isoproturon was purchased directly from market and was prepared in Double Distilled water.

4.1 Chemicals and reagents:

Mainly chemicals used in all these experiment which are following:

- Fly ash obtained from Ropar power plant.
- Strong oxidant H_2O_2 (30% V/v,) was used
- H_2SO_4 (0.1N) and NaOH (0.1N) were used for adjusting the pH of sample
- Double Distilled water was used for making the solution of sample throughout the process.

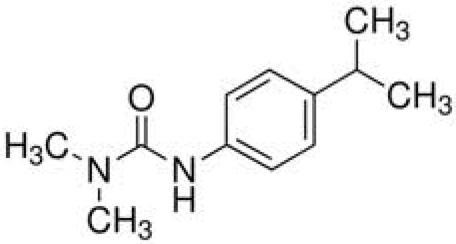


Fig 4.1 Structure of isoproturon

4.2 Instruments used:

pH meter: pH of the solution was monitored by using a digital desktop, pH meter (CP 901) from Century Instrument Company and pH was adjusted with the help of 0.1 N NaOH and 0.1 N HCl. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

Spectrophotometer: The spectrum was taken with UV-visible Spectrophotometer by Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer.

Magnetic stirrer: Magnetic stirrer was used during experimentation to solve the problem of mixing and solution remains in suspension.

Air sparger: Air is continuously supplied during experiments in UV reactor as well as solar experiments in order to oxidize the organic matter.

Filtration: After photo catalytic treatment by photo reactor, effluent sample were filtered through syringe filters having Millipore filters of 0.45 µm pore size.

UV chamber details: UV fenton treatment of isoproturon was performed in batch experiments in UV chamber rectangular in shape having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of wood. Roof of the reactor was fitted with seven UV tubes (36 Watt each) in parallel. Temperature inside the reactor was maintained by an exhaust fan. Four magnetic stirrers were fitted in the reactor to carry out the photo catalytic reaction in slurry mode.

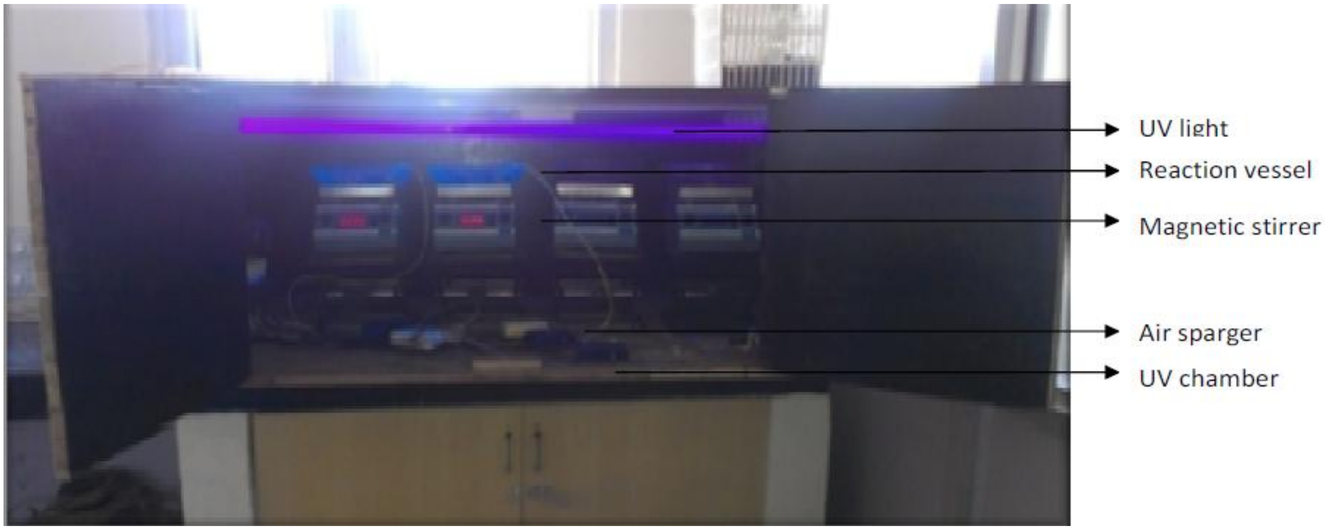


Figure 4.2 Photo reactor at lab scale during photocatalytic treatment

Small pond glass reactor: Small scale reactor type setup is made in which we use glass bowls covered with clean film. Magnetic bead is used to keep the reaction in suspension and aerators are used for providing aeration. Glass bowls were used for the Fenton reaction having a capacity of 1000 ml. Fig. 4.2 shows picture of the reactor.

Fig (5.4) Small pond glass reactor vessel in (a) UV light (b) solar light

4.3 Preparation of solution

4.3.1 Stock solution:

The stock solutions were prepared by adding a known amount of compound into a small amount of double distilled water in a 1-liter amber coloured volumetric flask to protect it from light and filling it to the mark with double distilled water. Stock solution is kept overnight for stirring for dissolving as isoproturon is not easily dissolved into water. Before the experiments could be performed, it was necessary to choose the appropriate concentration of compound solutions. For most of the experiments, stock solutions of 25 mg/L concentration were prepared by dissolving 25 mg isoproturon in double distilled water and make the solution quantity to 1 L.

4.3.2 Hydrogen peroxide:

Hydrogen peroxide (30% w/v) was obtained from Ranbaxy Laboratories, having molecular weight of 34.01. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg. Hence for adding 4.4 mM of H_2O_2 solution, 500 µl of H_2O_2 solution was taken in 1 L of stock solution or 100 µl of peroxide solution in 200 ml of stock solution.

4.4 Degradation of compound

4.4.1 Solar Photofenton: Isoproturon solution of 25mg/L was prepared by double distilled water. 200 ml of sample taken in small pond reactor, 1 gm of fly ash and 10 µl of H_2O_2 were added, air was also supplied by the aerator during experiment. Set up was placed in sunlight. Sample was taken in intervals of 5 min for first 15 min and later after every 15 min for 180 min and filtered from 0.45 micron syringe filter. The concentrations of these samples were detected by Spectrophotometer.

4.5.2 Fenton + UV : The experimental condition was same as in above , the only difference was UV chamber. In case of UV fenton, complete setup (photo reactor) was placed in UV chamber and the sample was taken in intervals of 5 min for first 15 min and later after every 15 min for 180 min. The concentration of these samples were detected by Spectrophotometer.

4.5.3 Dark fenton: The experimental condition was same as in photo fenton , the only difference was that in this case complete setup (photo reactor) was placed in dark away from light and the sample was taken in intervals of 5 min for first 15 min and later after every 15 min for 180 min. The concentration of these samples were detected by Spectrophotometer.

Chapter 5

Resuts and Discussion

Isoproturon (IPU), N,N-dimethyl-N′-[4-(1-methylethyl)phenyl] urea is a herbicide used for pre- and post emergence control of many broadleaf weeds in spring and winter wheat, barley and winter rye (**Fournier et al., 1975**) having λ_{max} 239 nm.

5.1 Standard curve of isoproturon:

Standard curve for isoproturon is prepared by plotting the graph between varying known concentration ranging from 0mg/L to 30mg/L and its absorbance at 239 (figure 5.1). From this graph we can calculate unknown concentration for solution. Value of R^2 is 0.998 and slope is 0.051

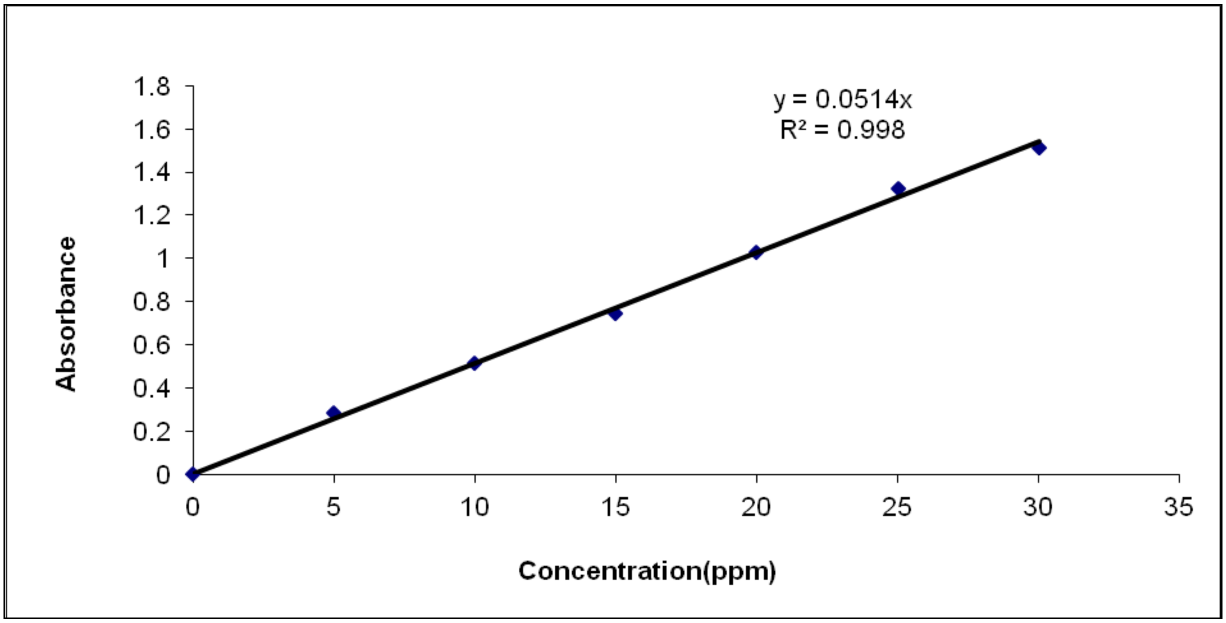


Fig 5.1 standard curve of isoproturon

5.2) Preliminary studies:

Preliminary experiments were carried to check whether only fly ash or only hydrogen peroxide or solar light is sufficient to carry out the degradation process. It was found out that there is no degradation when three main components of solar photo fenton are used alone. Fig 5.2 shows the effect of only fly ash, H_2O_2 , sunlight. Thus proposing some advanced treatment in combination with above treatment options for complete removal of herbicide from the solution.

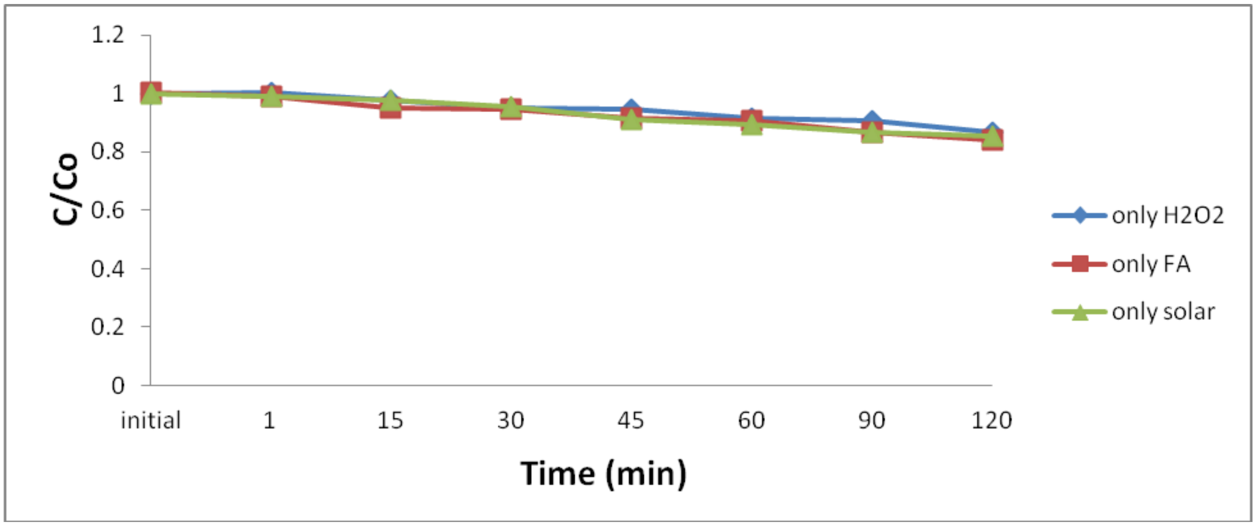


Fig 5.2 Effect of only fly ash(FA), only H_2O_2 and only sunlight

5.3 Dark fenton studies:

5.3.1 Effect of fly ash dosage: Experiment were performed in dark ie set up was covered with alluminium foil to make it away from light and it is placed on magnetic stirrer so that proper mixing takes place. Fly ash dose was varried from 1gm to 6 gm to check the value at which maximum degradation takes place. There is very little degradation in dark fenton even when fly ash is varried as shown in Fig 5.3. Fenton reaction rates are strongly increased by irradiation with UV/visible light **(Ruppert G.et al., 1993; Sun and Pignatello, 1993**). During the reaction when there is no light, Fe^{3+} ions are accumulated in the system and after Fe^{2+} ions are consumed, the reaction practically stops. But when light is present there is Photochemical regeneration of ferrous ions (Fe^{2+}) by photoreduction of ferric ions (Fe^{3+}) which is the proposed mechanism for fenton reaction (**Faust and Hoigné, 1990**). The new generated ferrous ions reacts with H_2O_2 generating a second HO*radical and ferric ion, and the cycle continues as shown in above reactions.

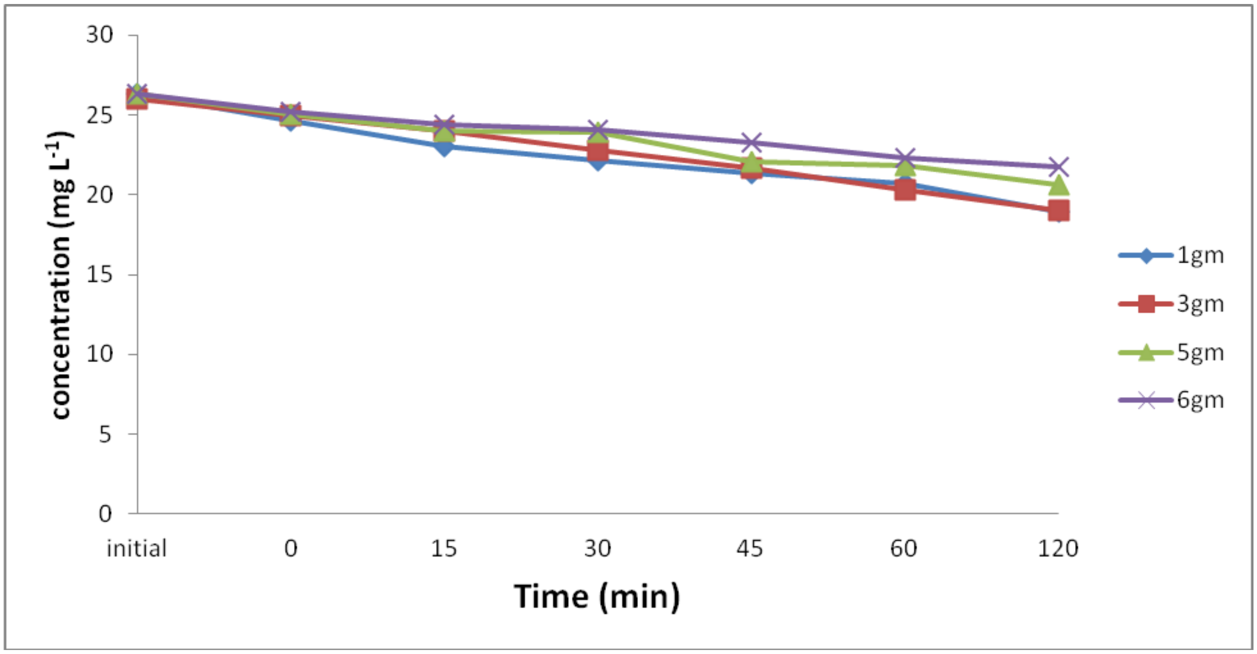


Fig 5.3 Effect of fly ash dosage in dark fenton (H_2O_2 10mM; pH 2)

5.3.2 Effect of amount of Hydrogen peroxide

The effect of amount of H_2O_2 is varried for degradation of isoproturon in dark fenton reaction as presented in fig 5.4. It is observed that the degradation increases on increasing the amount of H_2O_2 and after that attained a optimum value at H_2O_2= 10mM. Thereafter,degradation decreases on increasing the amount of H_2O_2. It is explained on the basis that more H_2O_2 molecules are available to react with Fe^{2+} ions, which increases the number of OH* radicals. Therefore,the rate of reaction also increases but on further increasing the H_2O_2, reaction decreases as all the OH* radicals are consumed by the H_2O_2 as shown in above reactions and there is very less OH* availabe which will slow down the process but there is less degradation as compare to solar fenton reaction due to less formation of OH* in dark as compare to formation in visible light.

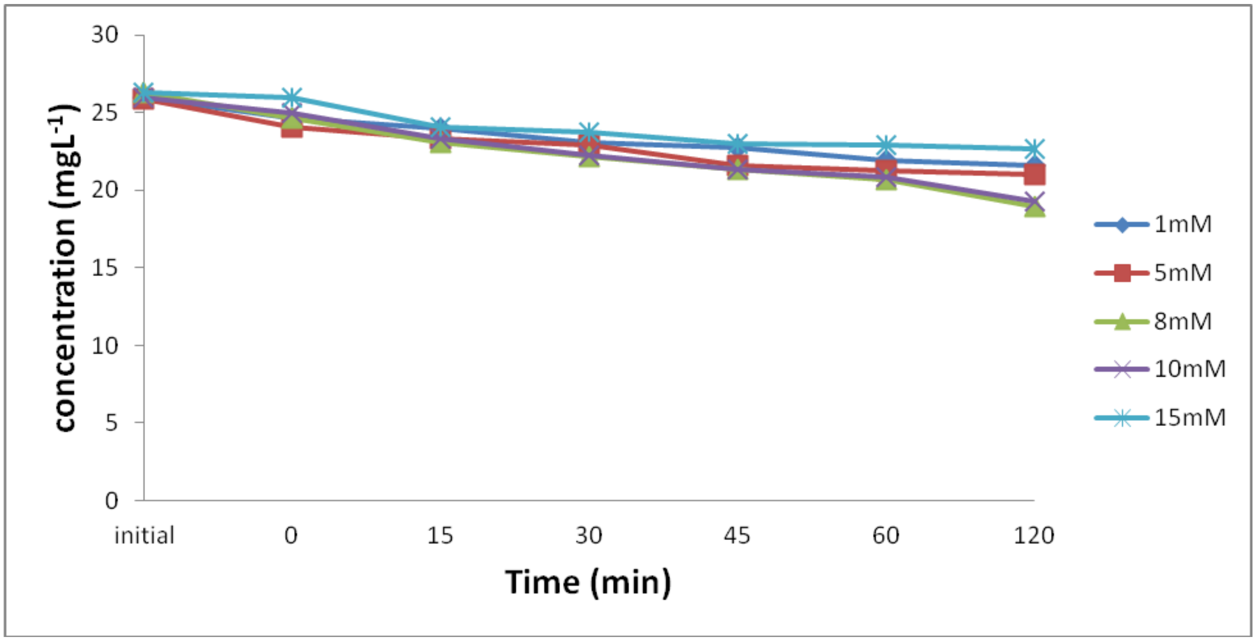


Fig 5.4 Effect of amount of H_2O_2 in dark fenton (fly ash 1gm ; pH 2)

5.3.3 Effect of pH

The effect of pH on isoproturon degradation was investigated in the pH range 1 to 5 but best was observed at pH 2 when other parameters were kept constant (fly ash 1gm ; H_2O_2 10mM) shown in fig 5.5 . In the dark, the reaction has been observed to slow down relative to the solar photo-Fenton system after depletion of H_2O_2 because reconversion of Fe^{3+} to Fe^{2+}, necessary for the subsequent production of OH* radicals is stopped.

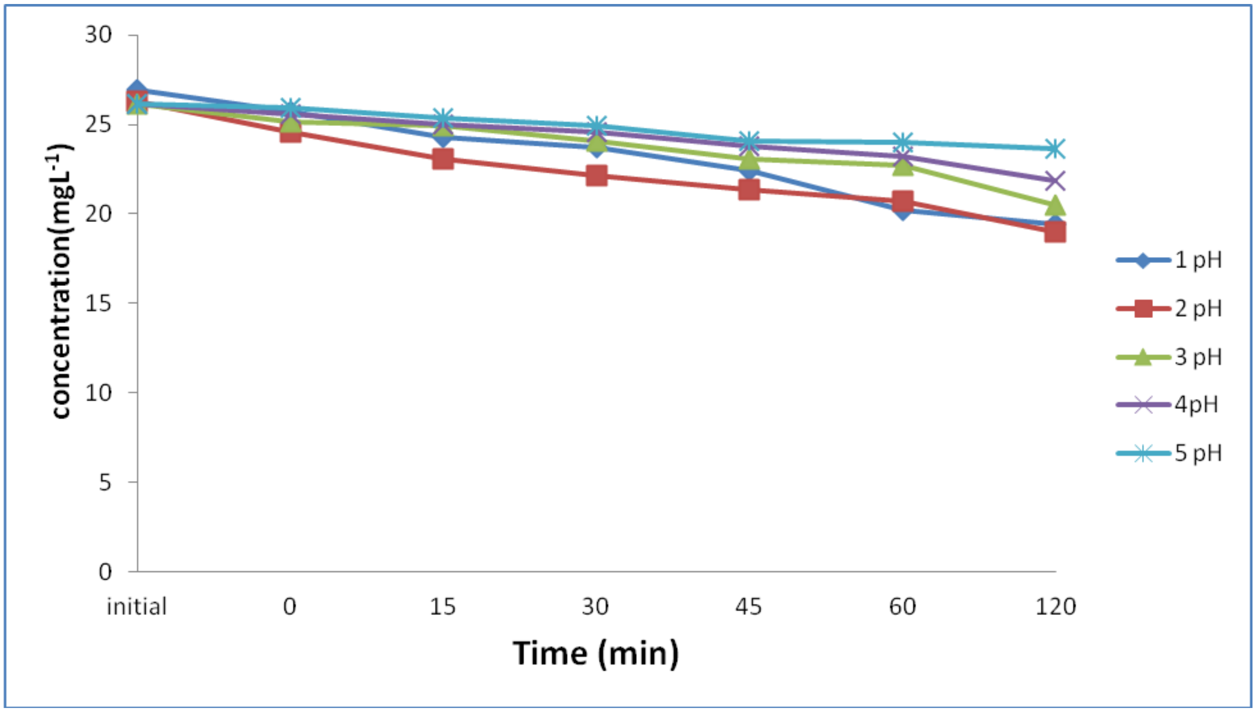


Fig 5.5 Effect of pH in dark fenton reaction(fly ash 1 gm; H_2O_2 10mM)

5.4) Solar photo fenton studies

5.4.1) Effect of fly ash dosage – Fly ash was used in varying concentrations ranging from 0.25gm to 5 gm during the photo Fenton treatment process for the optimization of the concentration. The amount of fly ash in stock solution is important parameter influencing the oxidation processes. Fly ash dosage act as catalyst, enhance the oxidation process. The results shown in Fig 5.6(a) depicted that increased fly ash dosage is increasing pesticide removal but upto certain point after that it start decreasing. Although by increasing fly ash dosage from 0.5 gm to 7gm, degradation of pesticide decreases. It may be explained by redox reaction that OH* scavenged either by the reaction with hydrogen peroxide or by the reaction with Fe^{+2} as expressed in the equations (**Malik P.K. and Saha S.K., 2003**):

$$H_2O_2 + OH^* \rightarrow H_2O + OH_2^*$$
$$Fe^{+2} + OH^* \rightarrow OH^- + Fe^{+3}$$

The maximum degradation of 92% was achieved at 1gm fly ash dosage within reaction time 180 min. The less degradation observed at High fly ash dosage may be because of less production of OH* for the oxidation process. Hence, 1 gm dosage of fly ash is used as an optimum dose. Fig 5.6(b) shows %age degradation of isoproturon by varying the amount of fly ash.

Fig 5.6 (a)

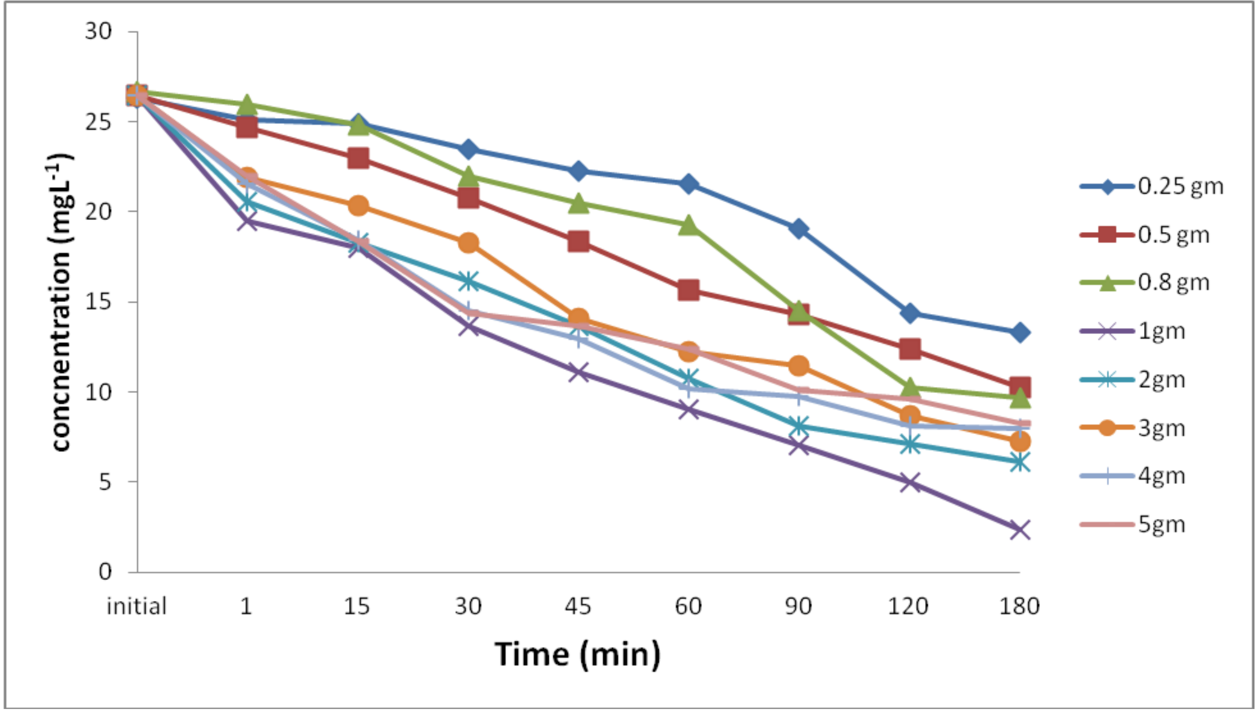


Fig5.6(b)

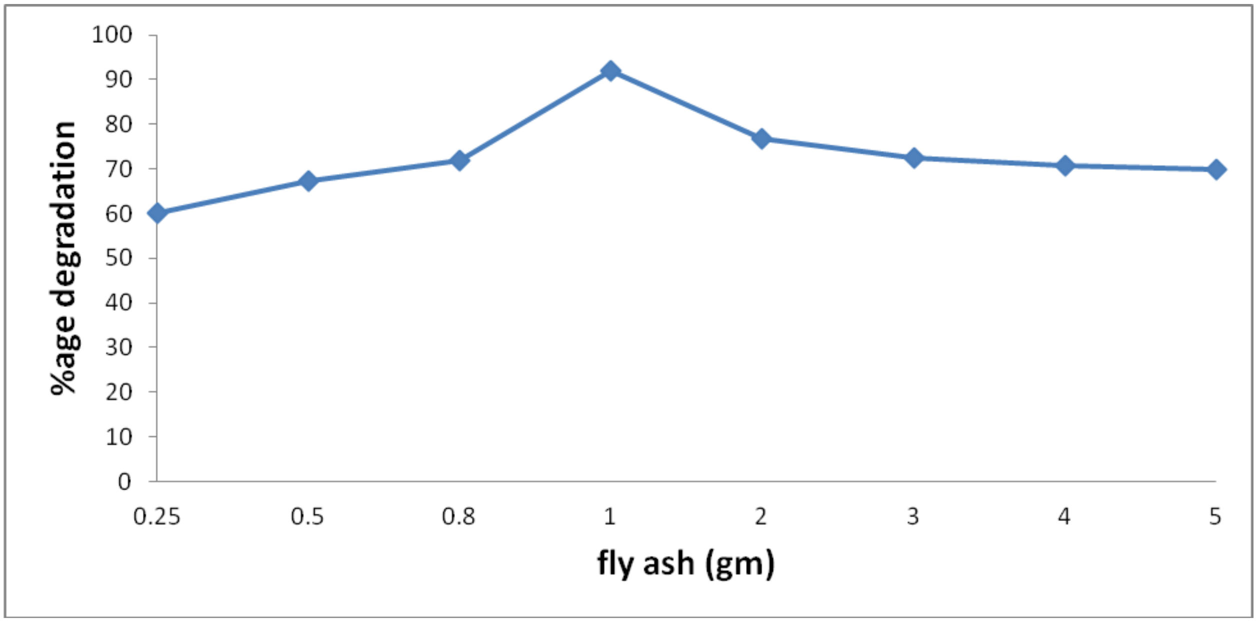


Fig 5.6(a) variation of fly ash with solar photofenton ; (b) %age degradation of isoproturon with solar photo fenton at varying fly ash(operating conditions: H_2O_2 10mM ; pH 2)

5.4.2 Effect of hydrogen peroxide

Fig 5.7(a) shows the degradation of isoproturon at different dosage of H_2O_2. The study was conducted to determine the optimum dosage of H_2O_2 for the best oxidation process. To optimize the dosage, H_2O_2 varies from 1 mM to 30 mM into the pesticide solution at fixed Fly ash and pH , pesticide removal increases with the increasing dosage of H_2O_2 till 10 mM after that percentage of removal decreases or becomes constant with the increasing dosage of H_2O_2 as shown in fig 5.7(b). This decrease is due to the fact of scavenging of OH* radicals by H_2O_2 **(Walling C.H., 1975)**, can be expressed by the equation:

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2^*$$

$$HO_2^* + OH^* \rightarrow H_2O + O_2$$

Effective degradation (91%) of isoproturon solution was achieved at optimum dose 10 mM of H_2O_2 within 180 min of reaction after which reaction was observed to be constant.

Fig 5.7 (a)

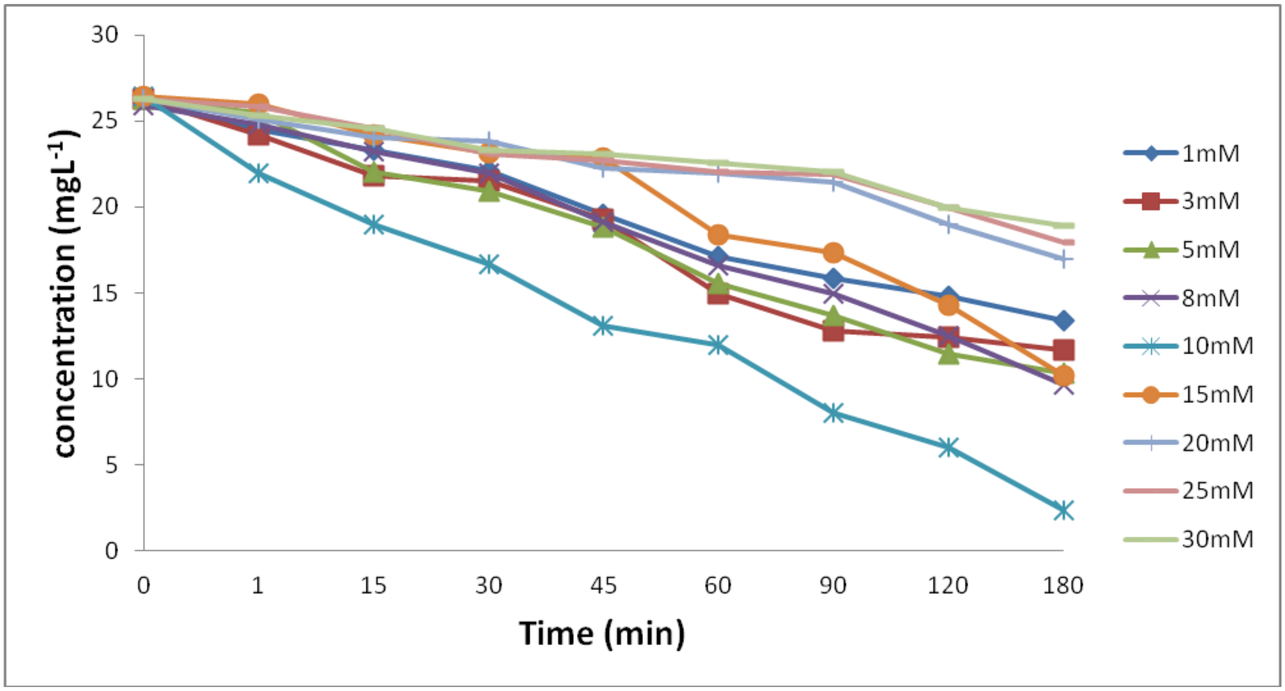


Fig5.7(b)

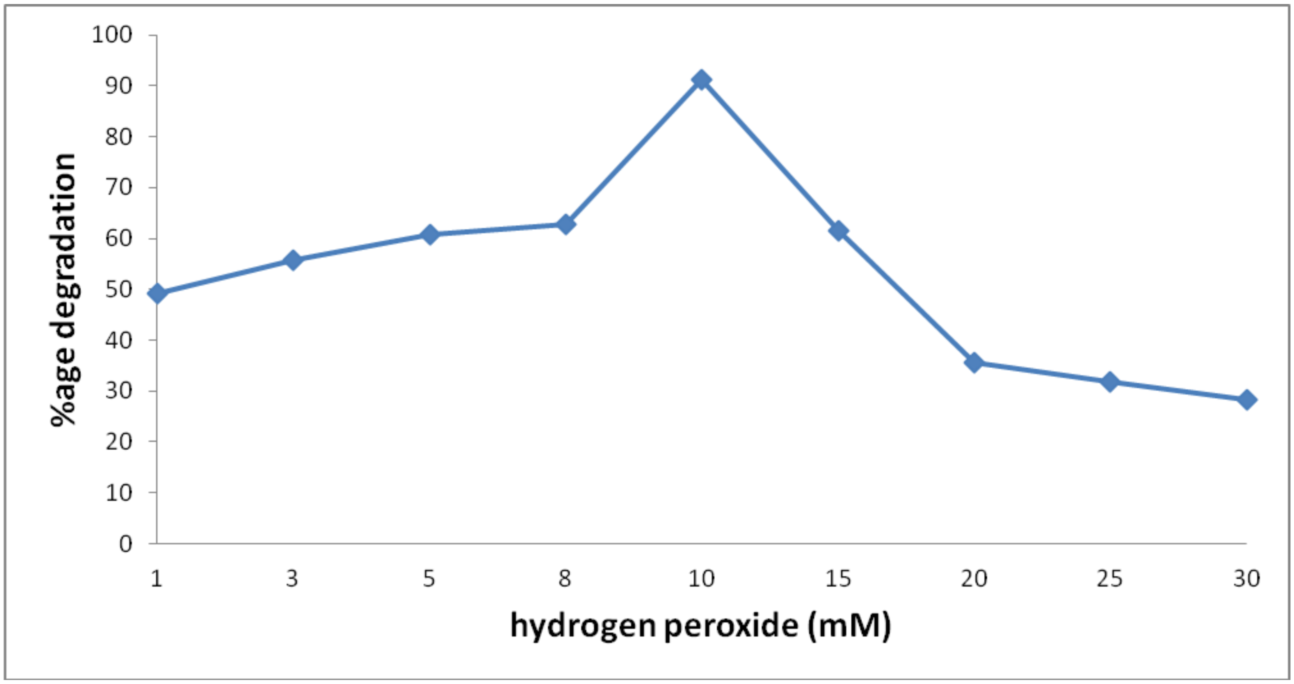


Fig 5.7(a)Effect of H_2O_2 on solar photo fenton reaction;(b)% degradation of isoproturon on solar photo fenton with varying amount of H_2O_2 (operating conditions: fly ash 1gm; pH 2)

5.4.3) Effect of pH

The effect of pH on the degradation of isoproturon by photo-Fenton processes is shown in Fig 5.8(a). The results confirmed that pH significantly influences the degradation of isoproturon. The experiments were carried out at different pH that varies from 1 to 6. The reaction has completed in 180 min under controlled pH and constant dose of fly ash(1gm) and H_2O_2 (10 mM). At low pH, 1 percentage removal of pesticide solution was very less and also percentage removal decreases with increasing pH i.e. 4 to 6. From the figure 5.8(b) it can be easily depicted that maximum degradation achieved at both pH 2 and 3 but pH 2 was used as a optimum pH . At lower pH 1, isoproturon removal was less because reaction between hydrogen peroxide and iron is seriously affected resulting, reduction in the OH* radical production. At lower and higher pH isoproturon removal was less also because of hydroxyl radicals scavenging of H+ ions (**Spinks J.W.T. and Woods R.J., 1990**)

$$OH^* + H^+ + e^- \rightarrow H_2O$$

Fig 5.8(a)

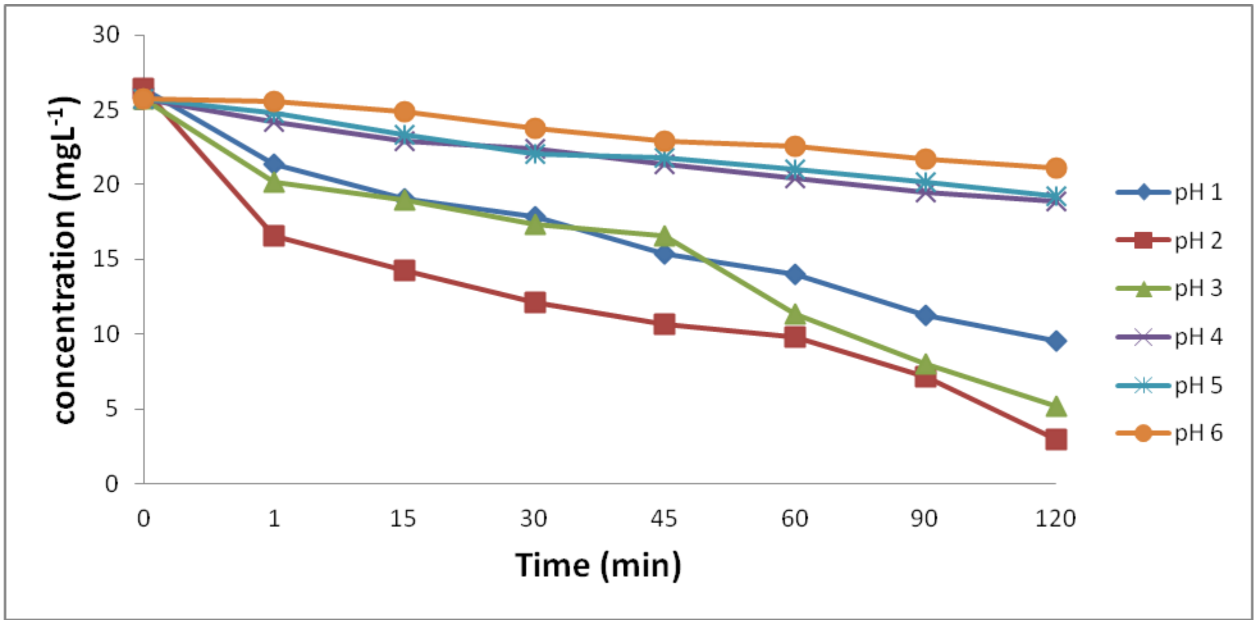


Fig5.8(b)

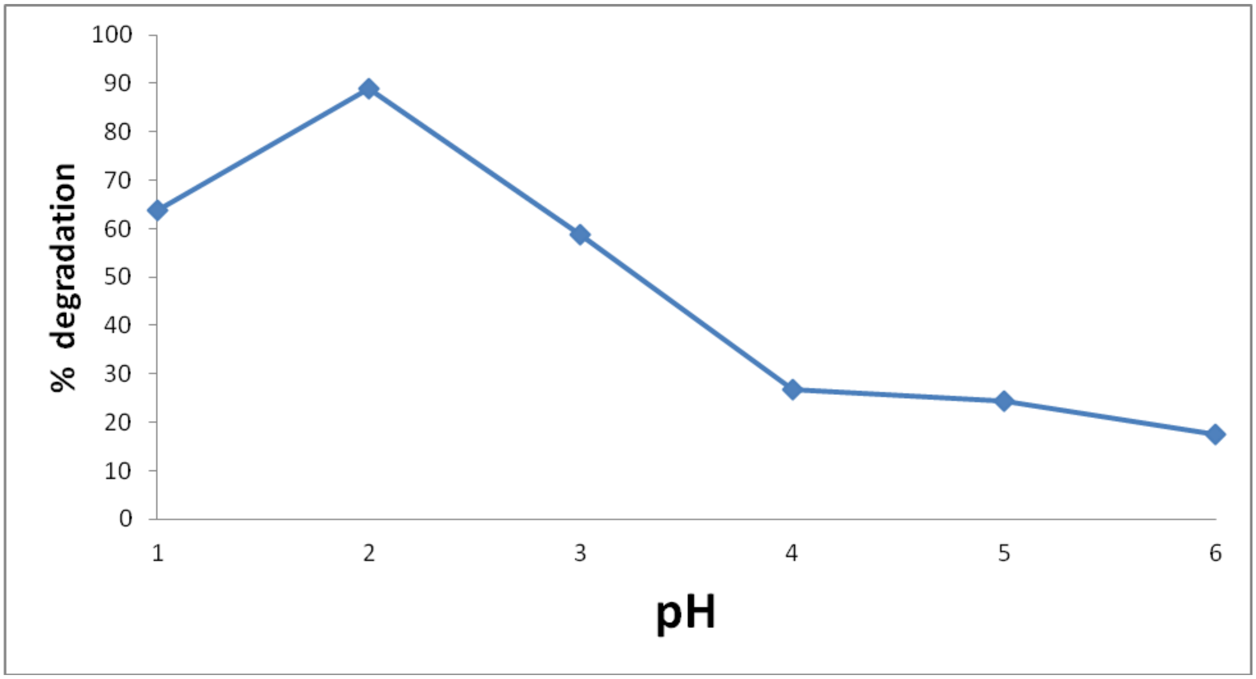
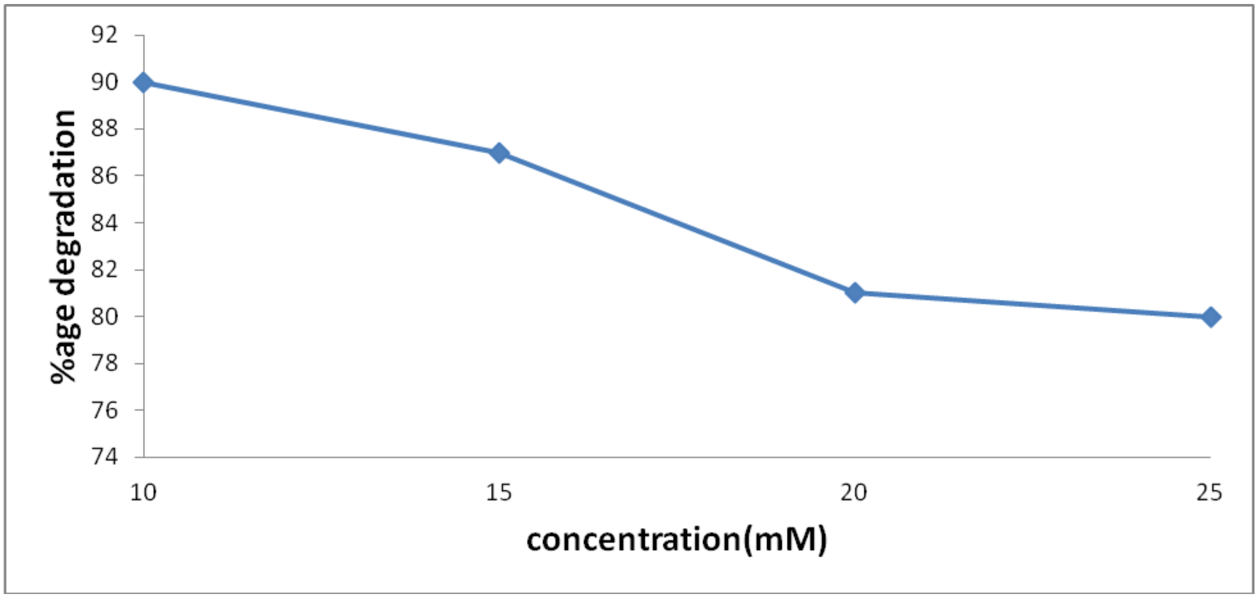


Fig 5.8(a) Effect of pH on solar photo fenton reaction; (b) % degradation of isoproturon with solar photo fenton by varying pH(operating conditions: fly ash 1gm; H_2O_2 10 mM)

5.4.4 Effect of initial concentration of isoproturon

The effect of initial herbicide concentration on the solar photo fenton processes was observed, since pollutant concentration is an important parameter in wastewater treatment. The influence of the initial concentration is shown in Fig.5.9 , it is observed that the extent of degradation decreases with the increase in the initial pesticide concentration. The increase of pesticide concentration from 10 to 25 mg/L decreased the degradation from 99.0% to 81.0% for 60 mins. A higher concentration increases the number of herbicide molecules, not the HO* radical concentration, and so the removal rate diminishes. The optimum conditions for the degradation of isoproturon were observed at pH 2.0, 1.0 g fly ash and 10 mM H_2O_2. As the initial concentration of isoproturon was 10 mg/L ,99.0% degradation was achieved within a time of 60 minutes.



5.9 Effect of initial conc. of isoproturon(fly ash 1gm ; H_2O_2 10mM ; pH 2)

5.4.5 Effect of recycling of fly ash

25 mg/L methyl orange, 1.0 g of recycled fly ash, and 10mM H_2O_2 had a pH of 2.0. they were placed for solar fenton reaction to occur in reactor. The fly ash separated from the solution by filtration. Tap water was used to wash used fly ash, which was then dried at 100^0 and then cooled down. There was a fly ash weight loss of less than 2.5% after each batch, so before proceeding to the next batch, fresh fly ash was added to make up for the lost mass. 1.0 g fly ash loading was kept for each batch. Since the reducing carbon and iron content in FA may lower the degradation of isoproturon. It can be seen from Fig 5.10 that the fresh fly ash has a stronger catalytic ability than the recycled fly ash but if fly ash was given a heat treatment its catalytic ability was slightly increased. For the recycled fly ash, the degradation %age was

88% for 1st recycle but if given heat treatment it would increase to90%. The amount of iron compounds in the fly ash decreases with the number of times the fly ash is reused and also surface fouling of fly ash takes place which can be removed by heat treatment. So, fly ash can be used for the degradation of herbicides in wastewater, which meets the strategy of developing cycling economy by using the waste solid.

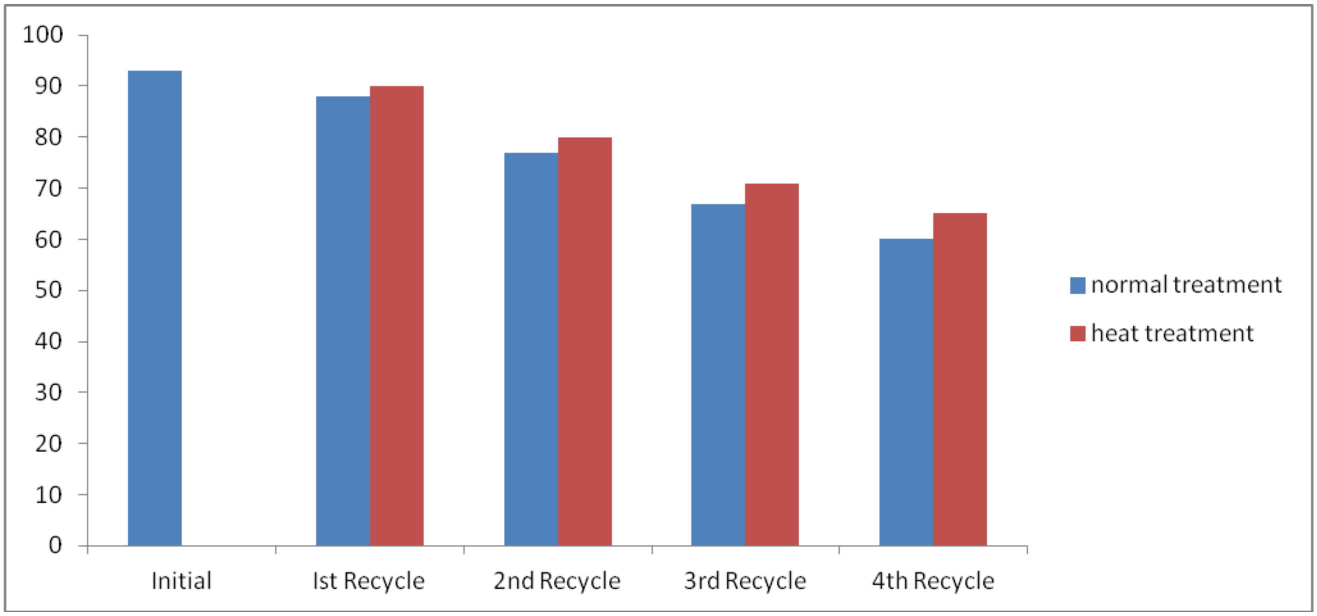


Fig5.10 Effect of recycling of fly ash (operating conditions:fly ash 1gm ; H_2O_2 10mM; pH 2)

5.5 UV Fenton reaction

5.5.1 Effect of fly ash dosage: The optimum concentration of fly ash is 1gm for degradation of isoproturon keeping other parameters constant (H_2O_2 10mM ; pH 2) under UV light. We can observe that degradation under UV is less as compared to solar fenton process due to the fact that fenton treatment works best in solar light as it have both components visible and UV light available in sunglight rather the only UV light.

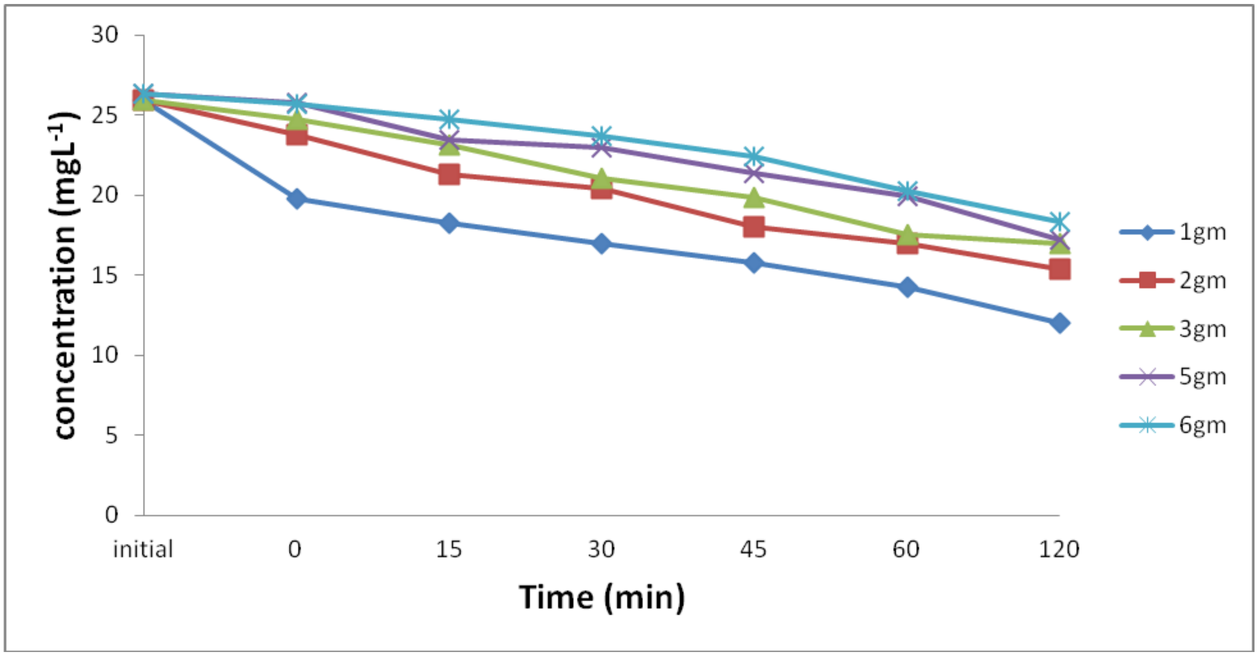


Fig 5.11 Effect of fly ash dosage on UV fenton treatment (H_2O_2 10 mM ; pH 2)

5.5.2 Effect of amount of H_2O_2

As shown in fig 5.12, the more H_2O_2 we added , the more degradation could be achieved. A degradation of 78% is achieved with 10 mM H_2O_2 within 120 min in UV fenton reaction. H_2O_2 concentration above 10 mM would not induce significant change in degradation rather it will lower down the degradation process.

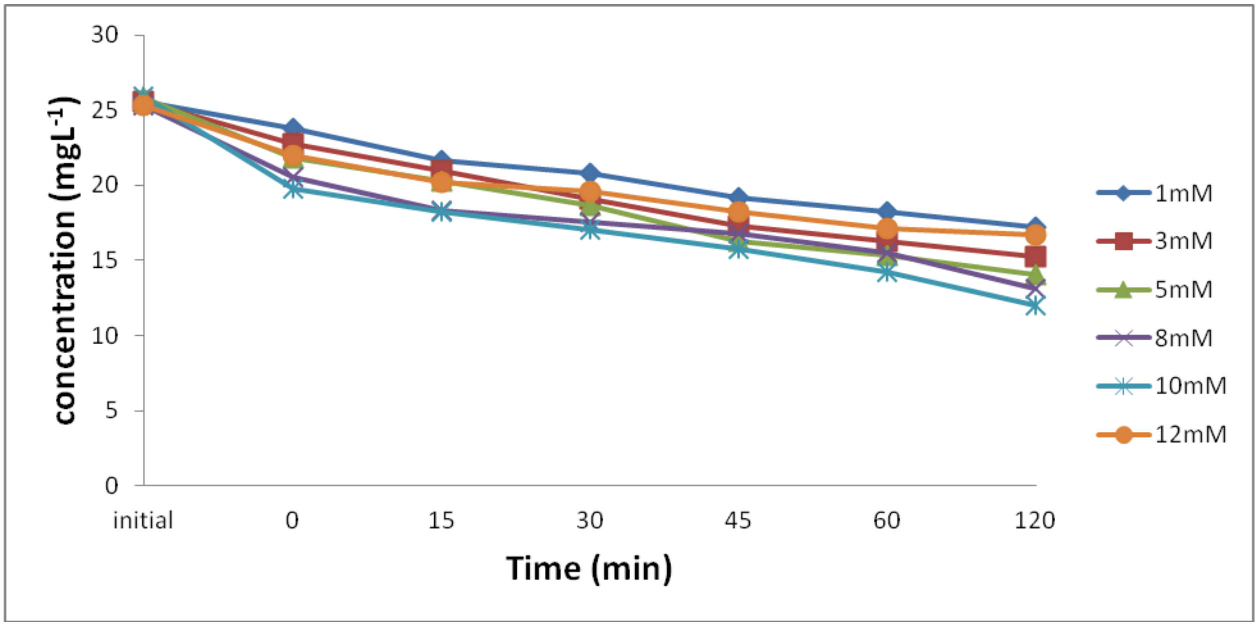


Fig 5.12 Effect of H_2O_2 in UV fenton process (fly ash 1 gm ; pH 2)

5.5.3 Effect of pH

The effect of pH on the degradation of isoproturon with fly ash 1gm and H_2O_2 10 mM was determined at a pH range of 1 to 5 and the results are presented in fig 5.13. Degradation is maximum at pH 2 and it decreases as we increase the pH. Degradation rate was less as compared to solar fenton reaction due to best stability of Fe^{2+} and H_2O_2 in solar fenton process.

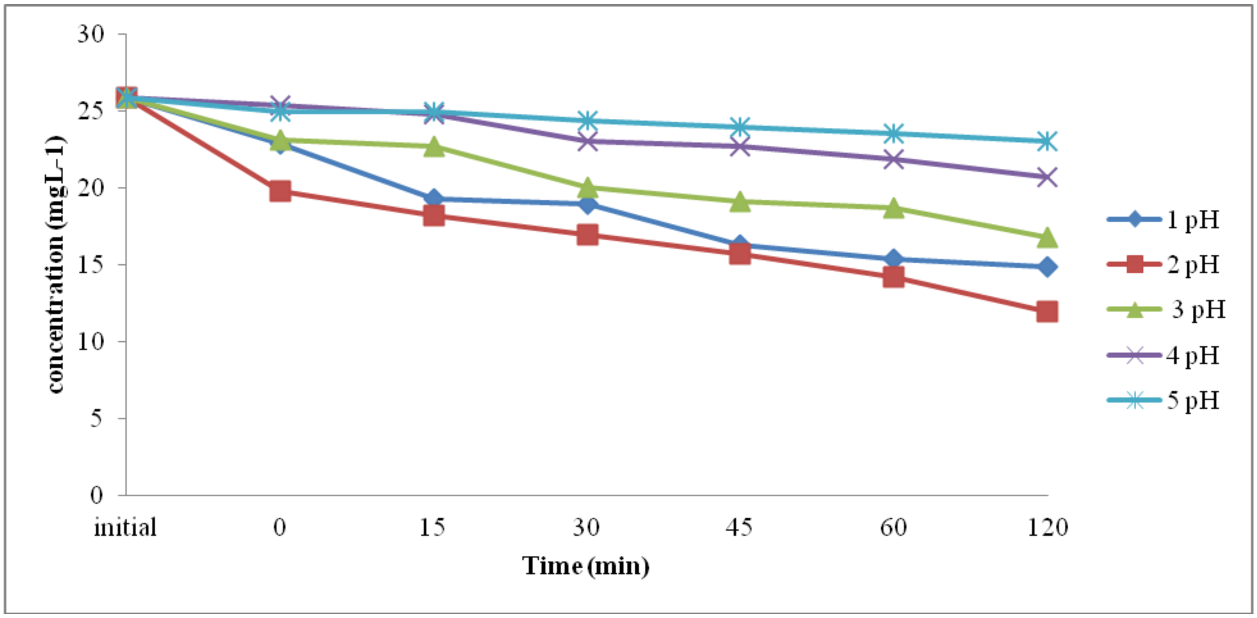


Fig 5.13 Effect of pH in UV fenton process (fly ash 1gm; H_20_2 10 mM; pH

5.6 Characterization of Fly ash and Leachate: Characterization of fly ash and leachate was done to confirm the leaching of metals. AAS (Atomic absorption spectroscopy) model GBC 932 AA was used to characterize fly ash and leachate using air-acetylene as a source of fuel for metals iron, lead, manganese and nickel and nitrous oxide-acetylene fuel is used for chromium. Sample was injected after digestion through capillary and hollow cathode lamp was used as light source. Results confirmed that significant amount of iron is consumed from fly ash as shown in (Table 5.1). Thus confirming its use as an iron source for a solar photofenton reaction. Thus negligible leeching of lead, chromium as well other metals guarantees its application in waste water treatment plants.

Table 5.1 Characterization of fly ash and leachate:

S. No.	Parameter	Test method	unit	Results	
				Fly ash	**Leachate**
1	Iron as Fe	APHA 22nd. Edn. 3111 B	mg/L	27.71	10.72
2	Lead as Pb	APHA 22nd. Edn. 3111 B	mg/L	0.53	<0.06
3	Nickel as Ni	APHA 22nd. Edn. 3111 B	mg/L	<0.10	<0.10
4	Chromium as Cr	APHA 22nd. Edn. 3500cr B	mg/L	0.29	<0.05

5.7 Absorption Spectra of isoproturon:

Absorption spectra of isoproturon (fig 5.14a) shows peaks in range of 200-300 nm which is in UV region thus confirming presence of refractory compounds but after treatment(fig 5.14b) the peaks become less which means compounds present are degrading after 180 minutes of treatment.

Fig (5.14 a)

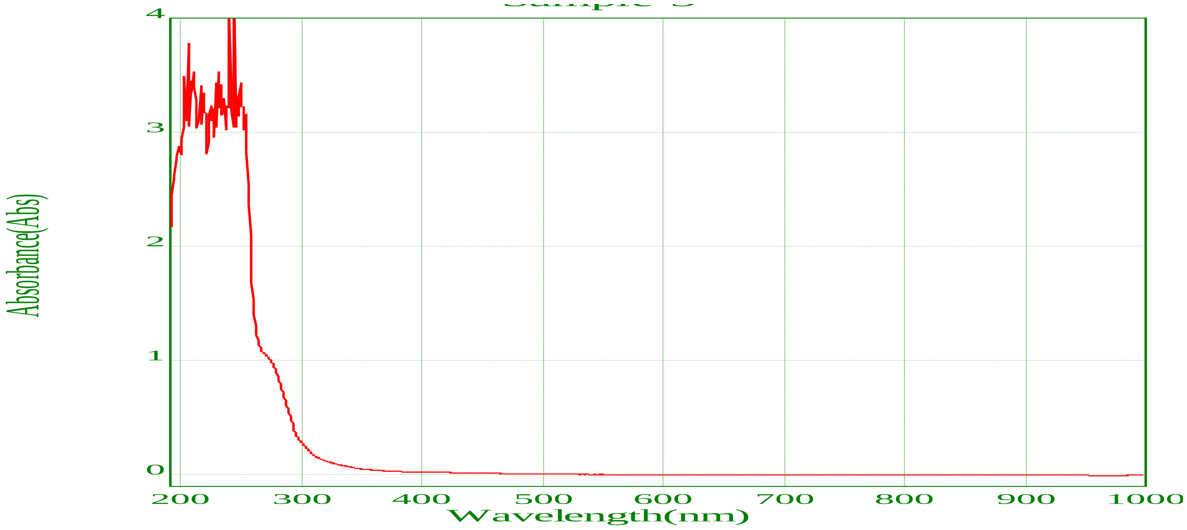


Fig (5.14 b)

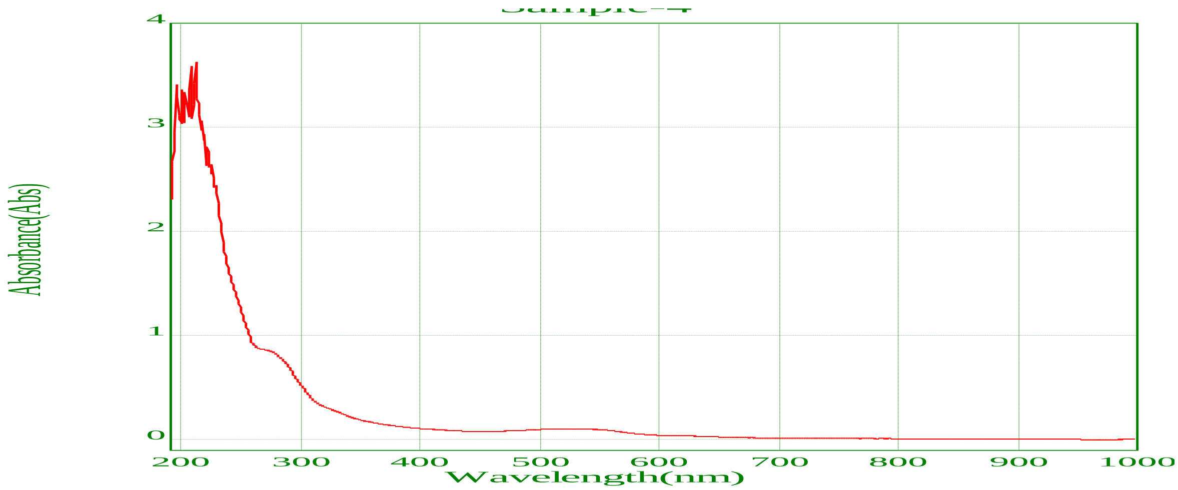


Fig 5.16(a) Absorption spectra of isoproturon before treatment (b) after treatment

Chapter 6

CONCLUSION

Fly ash-H_2O_2 systems can provide an advanced oxidation process for the purification of effluents containing pesticides. The novel process can be considered a simple, environment begnin, and economically feasible method for pesticide degradation. Fly ash is an alternative catalyst for the Fenton-like process, can be used to enhance the oxidation process, thus decreasing the consumption of H_2O_2 and generating less sludge. For the 200 mL, 25 mg/L isoproturon solution, the degradation ratio was 92.8% with 1.0 grams of fly ash, 10mM of H_2O_2, pH of 2. Fly ash can be separated from the solution and recycled as a catalyst for maximum of 3 times in order to avoid secondary pollution by sludge. Different advanced oxidation processes, i.e. dark fenton, solar photo fenton, UV fenton have been studied and their performances for the degradation of the isoproturon were compared. The experimental results presented demonstrate that dark fenton, solar photo fenton and UV Fenton reactions are suitable methods for the transformation of the isoproturon. However, the degradation rates were always higher for the solar photo-Fenton reactions when compared with the other two systems. Fig 6.1 shows comparison of three systems for degradation of isoproturon. Through this work we have found that the optimal concentrations of fly ash and H_2O_2 are 1gm and 10 mM, respectively, for the degradation of isoproturon in the solar photo-Fenton process. This study demonstrates the utility of the solar photo-Fenton system as a treatment method for the complete mineralization of non-biodegradable organic substances.

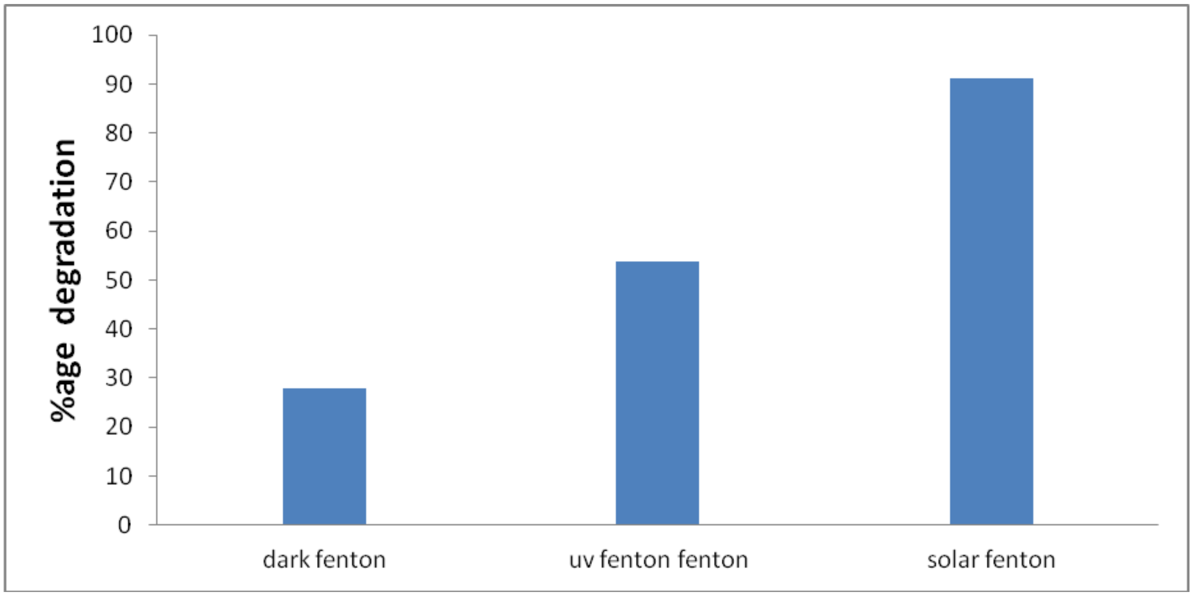


Fig 6.1 shows comparison of three Fenton processes

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