Potential use of foundry sand as heterogeneous catalyst in solar photo-Fenton degradation of herbicide Isoproturon

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in

Environmental Science and Technology

Submitted

By

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JULY 2014

CERTIFICATE

This is to certify that thesis entitled, "**Potential use of foundry sand as heterogeneous catalyst in solar photo-Fenton degradation of herbicide Isoproturon**" submitted by **Ms. Manpreet Kaur** in partial fulfilment of the requirements for the award of **Masters in Technology** Degree in **Environmental Science & Technology** at **Thapar University, Patiala** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.

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I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Potential use of foundry sand as heterogeneous catalyst in solar photo-Fenton degradation of herbicide Isoproturon**" has been carried out by me under the supervision and guidance of, **Mr. Anoop Verma, Assistant Professor & Supervisor,** ***Thapar University, Patiala***.

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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Last, but not least, I thank **God** for giving me strength to overcome difficulty, which crossed my way to be a pole star.

Thank you for making this a reality.

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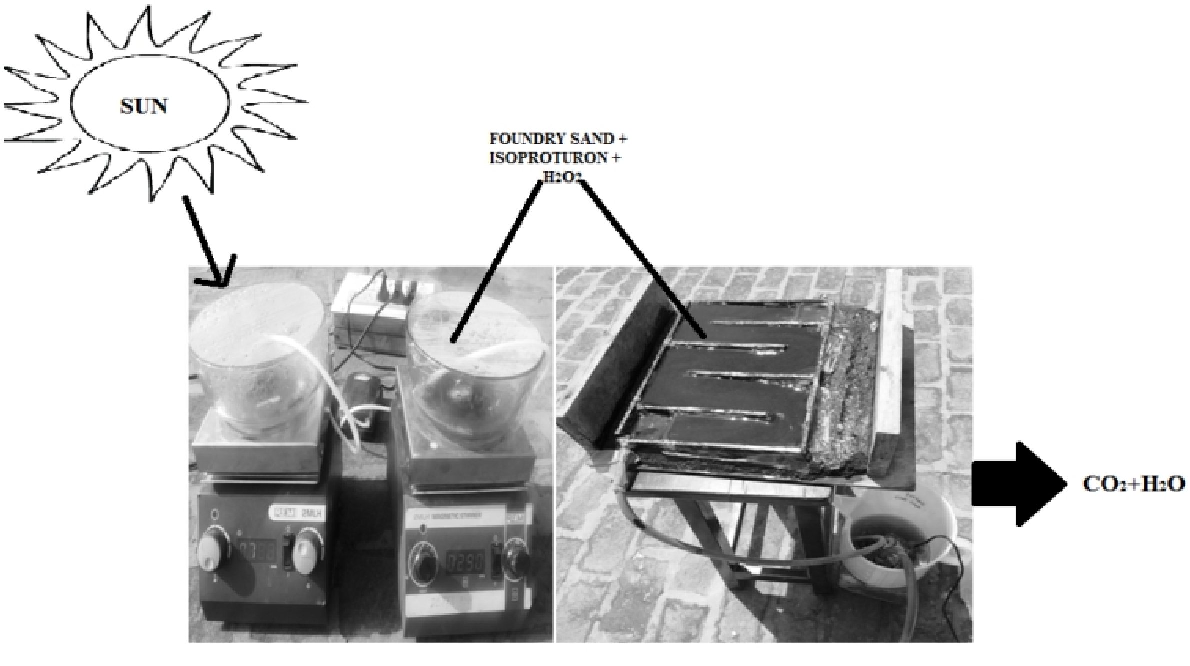
ABSTRACT

This study deals with employing foundry sand (FS) as new low cost iron source in heterogeneous photo-Fenton process for the degradation of herbicide isoproturon (IPU) in aqueous solution. The characterization of the FS by EDS confirmed presence of iron (23%) required for photo-Fenton and simultaneously confirmed absence of any heavy metals which may susceptible to leaching. The photo-Fenton effects of different reaction parameters like H_2O_2 concentration $[H_2O_2]_0$, operating pH, initial concentration of IPU $[C_0]$, FS dose, recycling of FS, effect of area/volume ratio were investigated. Results showed that the maximal removal efficiency were achieved when reaction parameters was $[H_2O_2]_0$= 2.2 mM, pH 3, FS dose=0.5 gL^{-1}, $[C_0]$ =25 mgL^{-1}. Under optimum condition, 97% degradation efficiency of IPU was achieved within 150 min of reaction. The catalyst recycling test was performed and FS was effectively recycled for 4 times with 20% reduction in degradation efficiency. SEM-EDS analysis of recycled FS confirmed morphology of FS unchanged. Solar baffled batch reactor (SBBR) with recirculation confirmed 70% degradation of IPU after 6 h.



Keywords: Foundry sand; Herbicide isoproturon; Photo-Fenton; Degradation; Mineralization

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Chapter 1

Introduction

Although pesticides have been detected in water since the 1950s, pesticide use has increased 50-fold since 1950 and 2.3 million tonnes of industrial pesticide are now used each year. The United Nations estimates that of all pesticides used in agriculture, less than 1 % actually reaches the crops. The remainder of pesticide used in agriculture results in a significant amount being transferred to natural waters and leads to deterioration of water quality. Figure 1 showing the different stages involved in pesticide cycle. 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 et al., 2009)**. Exposure to pesticides both occupationally and environmentally causes a range of human health problems increasingly linked to immune suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer **(Abhilash and Singh, 2009)**

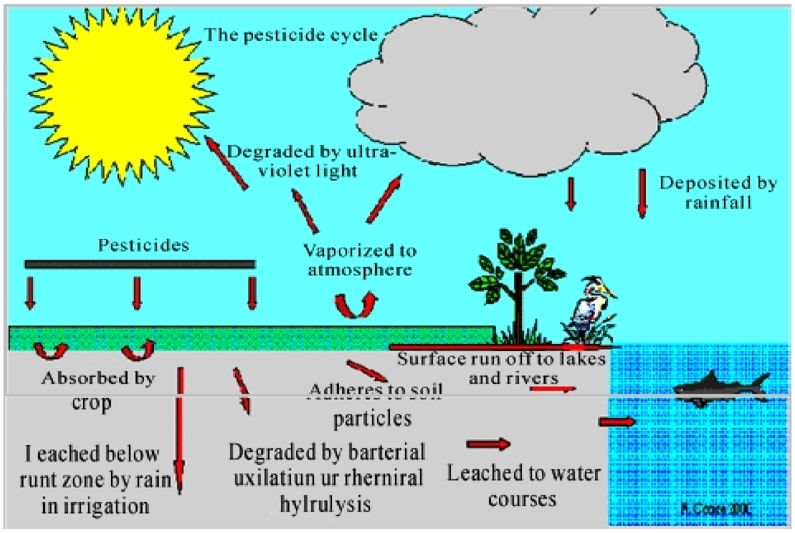


Figure 1. A scheme showing the different stages involved in pesticide cycle, source: website: The University of Reading, ECIFM, pesticides.

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)**.

As conventional biological treatments cannot effectively remove many of these toxic pollutants, this has led to a growing concern about their effect on human health and water pollution. Conventional treatment **(Guimarães et al., 2014)**, biological oxidation **(Guimarães et al., 2014)**, physiochemical processes are either incapable, inefficient for pesticide treatment or merely transferring the pollutants from one phase to another **(Guimarães et al., 2014)**. The presence and persistence of these non-biodegradable pesticides has motivated many researches to find alternate environment friendly solution for the treatment. 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)**.

1.1 Advanced oxidation processes

The advanced oxidation process (AOP) technology reported in Figure 2 could help to overcome the inability of conventional biological treatments for the effectively removal of pesticide pollution. Advanced oxidation process (AOP) offers the advantage of being insensitive to the toxicity of the pollutants and the possibility of fast treatments. In effect it can either achieve a complete mineralization of the organic contaminants to CO_2 and H_2O or transform them into less harmful or more biodegradable intermediates. Among the AOPs, those which produce hydroxyl radicals have been most successful **(Huston et al., 1991)** as this type of compound is strongly oxidative. 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**).

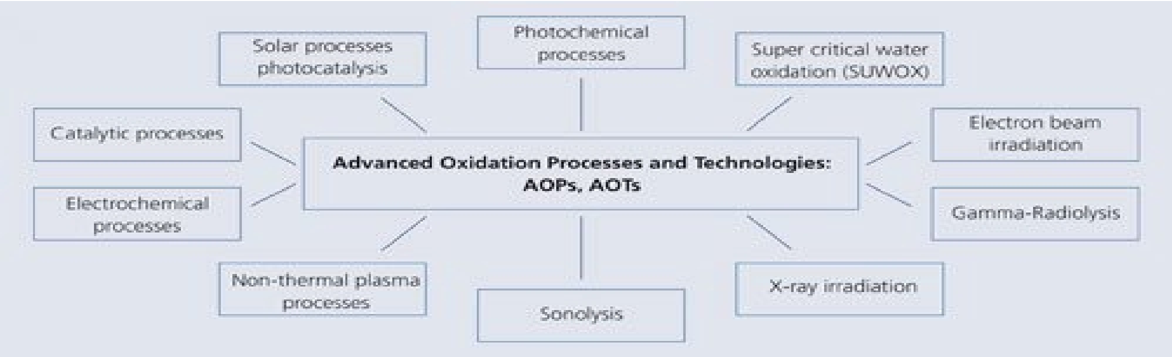


Figure 2. Different advanced oxidation processes

Hydroxyl radicals are not very selective, which is a useful attribute in wastewater treatment, but the production of a great number of transformation products (TPs) in route to complete mineralization can also be expected.

The effectiveness of H_2O_2 when in contact with a transition metal catalyst added as a soluble salt or as a solid, in Fenton or Fenton-like reactions, has been proven in the treatment of hazardous compounds in the aqueous phase **(Arnold et al., 1995, Gallard and Laat, 2001).** In particular, when ferrous sulphate is added to a H_2O_2 solution in Fenton systems, reactions that lead to the formation of hydroxyl radical ($OH^{\bullet}$) and numerous other competing reactions occur. Among these reactions, the production of hydroperoxyl radicals, the cycling of iron (III) to iron (II) and the quenching of $OH^{\bullet}$ by iron (II) and H_2O_2, occur, as summarised below **(Mohanty and Wei, 1993).**

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^{+} + HO_2^{\bullet} \quad (2)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \quad (3)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

$$HO_2^{\bullet} + Fe^{2+} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (7)$$

In addition the reaction of $OH^{\bullet}$ with organic substrates can lead to the formation of organic radicals, which might also be oxidised by Fe^{3+}, thus regenerating Fe^{2+} **(Gallard and Laat, 2001)**.

Photo-Fenton is one of the most promising advanced oxidation process (AOP) for pesticide degradation in waste water **(Ikehata and El-Din, 2006).** The Fenton and related reactions are viewed as potentially convenient and economical ways to generate oxidizing species for treating chemical wastes. In effect it can either achieve a complete mineralization of the pollutants to CO_2 and H_2O or transform them into less harmful or more biodegradable intermediates. When a metal catalyst is added, hydrogen peroxide (H_2O_2) most commonly used oxidizing agent generates free radicals.

Homogenous system generally offer high contaminant removal rates **(Kwon et al., 1999).** On the other hand it has significant disadvantage: the removal/treatment of water containing Fe ions at the end of wastewater treatment which is difficult and expensive. Heterogeneous catalysis, the catalyst can be easily recovered by sedimentation or filtration and further used or can be immobilized on inert support surfaces. Different types of solids can be used as heterogeneous catalysts. Among them iron powder and different iron oxides have been tested **(Lucking et al., 1998).** The catalytic activity can be related to the activation of hydrogen peroxide by iron leached from the solid catalyst and acting as homogenous catalyst. The main advantage in heterogeneous catalysis is the slow release of metal ions that limits undesired reactions **(Lucking et al., 1998).**

1.2 Foundry sand

Worldwide, Foundry sand produced in large amounts as an industrial by-product and creates problems for its disposal for the foundry industry. A few studies have been reported in literature regarding its reuse potential such as in environmental remediation as adsorbent for different pollutants **(Lee et al., 2004; Lee et al., 2004),** in agriculture **(Dungan and Dees, 2007)** and use it in construction material **(Siddique and Noumowe, 2008; Bakis et al., 2006). Molding sand,** also known as **foundry sand (FS),** is sand that when moistened or oiled tends to pack well and hold its shape. It is used in the process of sand casting. Foundry sand is an aggregate of sand, bentonite clay, pulverized coal or coal dust and water. Its principal use is in making molds for metal casting.

The largest portion of the aggregate is always sand, which can be either silica or olivine. There are many recipes for the proportion of clay, but they all strike different balances between mold ability, surface finish, and ability of the hot molten metal to degas. The coal typically referred to in foundries as sea-coal, which is present at a ratio of less than 5%, partially combusts in the surface of the molten metal leading to off gassing of organic vapours.

Table 1. Foundry sand sample chemical oxide composition, %

Constituent	Value (%)
SiO_2	87.91
Al_2O_3	4.70
Fe_2O_3	0.94
CaO	0.14
MgO	0.30
SO_3	0.09
Na_2O	0.19
K_2O	0.25
TiO_2	0.15
P_2O_5	0.00
Mn_2O_3	0.02
SrO	0.03
TOTAL	99.87

Most metal casting sand (FS) is high quality silica sand with uniform physical characteristics. It is a by product of the ferrous and nonferrous metal casting industry, where sand has been used for centuries as a molding material because of its unique engineering properties. In modern foundry practice, sand is typically recycled and reused through many production cycles. Industry estimates are that approximately 100 million tons of sand is used in production annually. Every year foundries generate 9 to 13 million tons of sand that is unfit for continued use in the mold making process and only small percent of waste sand are reused **(U.S. Environmental Protection Agency, 2002; Foundry Industry Recycling Starts Today (FIRST), 2006)**. The increasing foundry sand dumping costs and liabilities constitute a driving force for the adoption of novel methods for its reuse. In this view, the use of foundry sand as iron catalyst in heterogeneous photo-Fenton catalysis for degradation has been examined and to assess the efficiency of this particular catalyst, isoproturon (IPU) was chosen as model compound.

1.3 Isoproturon

To test the effectiveness of this particular catalyst, Isoproturon 3-(4-isopropylphenyl)-1,1dimethylurea was chosen as model compound. Isoproturon 3-(4-isopropylphenyl)-1,1dimethylurea is a selective herbicide used to control weeds in agricultural and non-agricultural sectors. It was considered as priority pollutant by the European Union (EU) (Directive 2008/32/EC) due to its high toxicity and also because of its low tendency to sorbs to soil, rendering it mobile in soil lead to extremely easy transport in environment and can therefore easily cause contamination to both surface and ground water. Its persistence leads to high pollution levels and therefore European Union recently restricted its usage. In surface water Isoproturon can be biodegraded or subjected to abiotic transformations **(Bending et al., 2007).** The herbicide isoproturon used for emergence control of annual grasses and broad-leaved weeds in spring and winter cereals. Its half life in water is 30 days (DoEReference: WS/45/1/1) thus have high tendency toward bioaccumulation. Isoproturon has been detected in both surface and ground water, quite persistent in water and hydrolyses very slowly. It is selective herbicide acting by inhibition of photosynthesis. This molecule can be transferred from soil to the aquatic environment by leaching and run-off **(Gooddy et al., 2002).**

There are a number of possible degradation treatments for pesticide remediation in the environment including Conventional treatment, biological oxidation and physiochemical processes. However, most of them are not applicable for degradation treatment because of being expensive, incapable, and inefficient for pesticide treatment and not always environmental friendly or they are merely transferring the pollutants from one phase to another. Thus, keeping the environmental concerns associated with isoproturon and other phenylurea herbicides in view, there is need to develop safe, convenient and economically viable methods for its remediation. The presence and persistence of these non-biodegradable pesticides has motivated many researchers to find alternate environment friendly solution for the treatment. The success of advanced oxidation process (AOP) heterogeneous as well as homogenous photo catalysis for the degradation of pesticide has been widely accepted in literature. Evidence for enhanced IPU degradation has stimulated the research aiming at to assess foundry sand (FS) efficiency as a heterogeneous catalyst in the Fenton remediation of isoproturon (IPU) contaminated water.

The **principal objective** of my study is to investigate the degradation of isoproturon (IPU) using foundry sand (FS) as a new low-cost iron source for the heterogeneous photo-Fenton process.

The study was undertaken with the following objectives:-

1. To estimate the potential of FS as an iron source for the treatment of IPU using photo-Fenton degradation.
2. Slurry/immobilized photo-Fenton degradation studies using FS for the treatment of IPU.
3. Process optimization by varying the parameters like oxidant dose, iron dose, pH, initial concentration of pollutant, etc.
4. Design/Fabrication of fixed bed using foundry sand and other materials.
5. Reusability studies of the FS in context to the degradation of compound.

To the best our knowledge, this is the first reported study towards the use of foundry sand as heterogeneous catalyst in photo-Fenton degradation of pesticide. This would be of economic interest keeping in mind the high costs required for disposal of foundry sand which we are using as a catalyst that is commonly considered as a waste.

Chapter 2

Review of literature

2.1 Pesticide pollution

The pesticides belong to a category of chemicals used worldwide as herbicides, insecticides, fungicides, rodenticides, molluscicides, nematicides, and plant growth regulators in order to control weeds, pests and diseases in crops as well as for health care of humans and animals. Reports from Delhi, Bhopal and other cities and some rural areas have indicated presence of significant level of pesticides in fresh water systems as well as bottled drinking mineral water samples as shown in below given figures 3, 4 & 5. At present, India is the largest producer and consumer of pesticides in Asia and ranks 12th in the world for the use of pesticides with an annual production of 90,000 tons (**Abhilash and Singh, 2009**). 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 et al., 1999**).

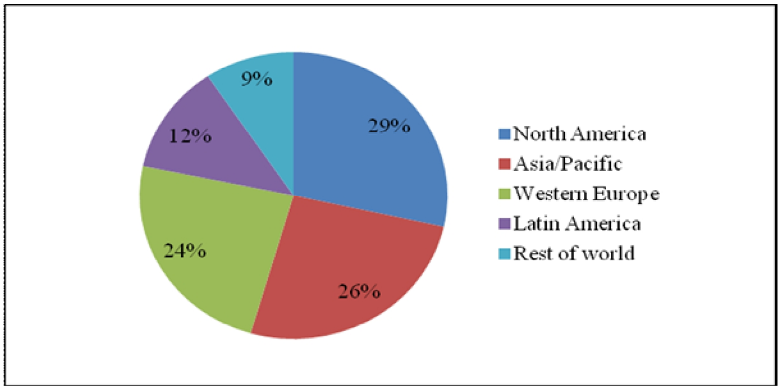


Figure 3. World's scenario of agrochemical sales by region (Dewar, 2005)

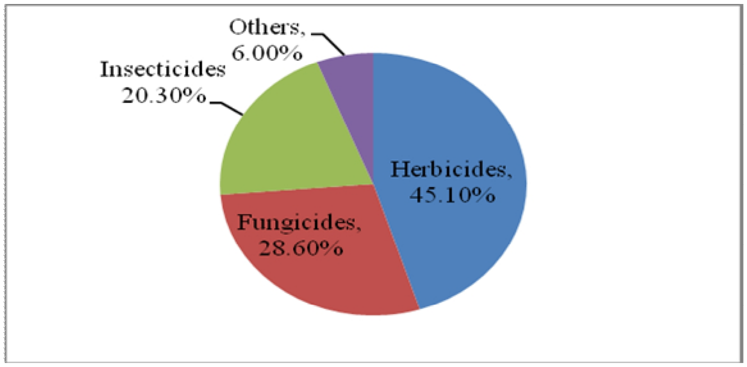
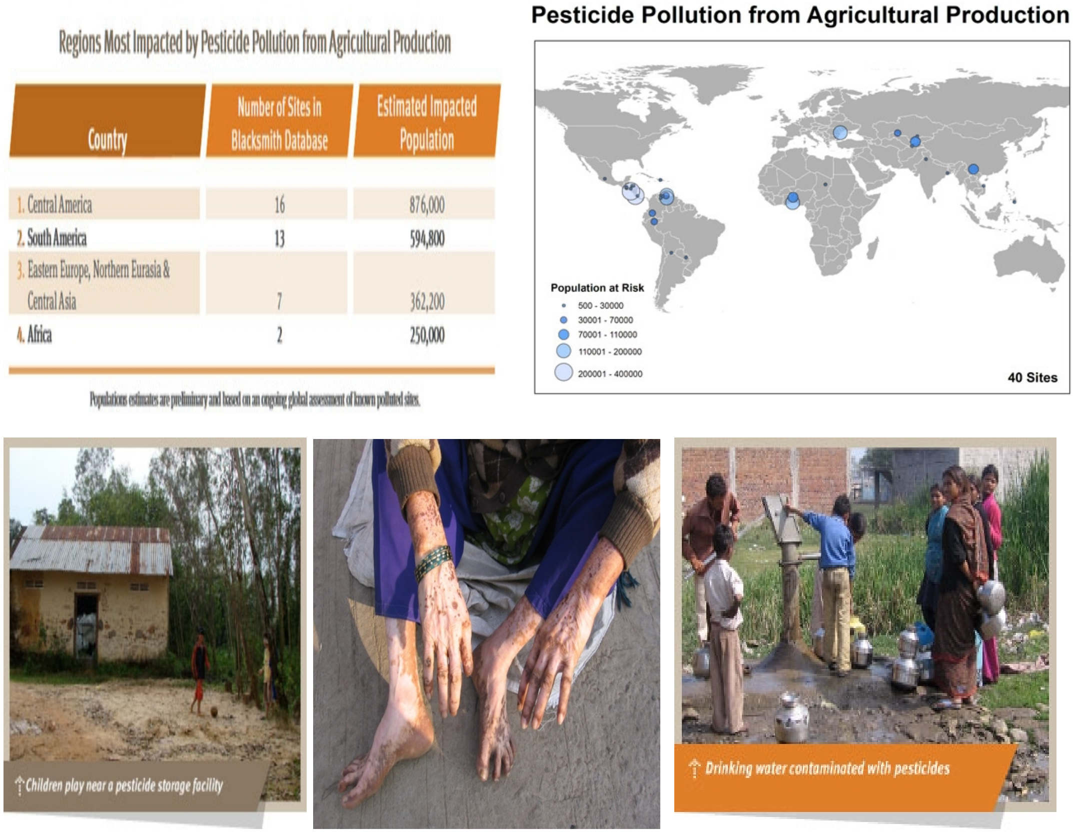


Figure 4. World's scenario of agrochemical sales by product category (Dewar, 2005)



Regions Most Impacted by Pesticide Pollution from Agricultural Production

Country	Number of Sites in Blacksmith Database	Estimated Impacted Population
1. Central America	16	876,000
2. South America	13	594,800
3. Eastern Europe, Northern Eurasia & Central Asia	7	362,200
4. Africa	2	250,000

Populations estimates are preliminary and based on an ongoing global assessment of known polluted sites.

Figure 5. Shows regions most impacted by pesticide pollution and their effects.

2.2 Harmful effects on human beings

The wide use of pesticides has been found to affect not only the workers who are handling them but also to the rest of population who are not using them. Exposure of the pesticides to the human beings could occur through:

- inhalation of pesticide contaminated air
- drinking of the contaminated water
- ingestion of the pesticide contaminated food
- dermal contact
- across the placenta

The exposure of the pesticides to human beings can be described in several ways like accidental or incidental, acute or chronic, intentional or unintentional and occupational or non-occupational. It has also been reported that about 3 million people worldwide are poisoned and about 200,000 die because of this poisoning **(WHO, 1990; FAO, 2000)**. This dilemma is predominantly happening in the developing countries where some pesticides banned by developed countries are still being used **(Wilson and Tisdell, 2001)** and where the development of distribution channels remains poorly organized. A study conducted by the "Directorate General for Health and Consumer Protection" of the European Union showed that 49.5% of samples of food plants of French origin tested contained pesticide residues with 8.3 % at rates higher than the maximum allowed **(Tron et al., 2001)**. This alarming fact is confirmed by measuring levels of pesticides found in the human body. Various studies from people from different countries showed that 99% of people tested stocked DDT in their fat tissues **(Turusov et al., 2002)**. Moreover, the presence of many pesticides has been detected in breast milk, sometimes at concentrations exceeding the acceptable daily intake for infants **(Romero et al., 2000)**. The exposure of the pesticides to the human beings may result in different types of the harmful symptoms starting from the carcinogenic effects to the effects on the digestive, reproductive and respiratory systems in human beings. Some of the harmful effects of the pesticides on the human beings are: There are evidences that high-dose exposures of the pesticides may affect the immune system **(Caress and Steinemann, 2003; Weselak et al., 2007),** increased risk of allergy **(Weselak et al., 2007)** and multiple chemical sensitivity **(Caress and Steinemann, 2003)**. Cancer is considered as one of the most common end point while studying the harmful effects of different chemicals on the health. Many of the previous research have indicated the possible carcinogenic effects of the pesticides which can cause cancer in brain, kidney, prostate, pancreas, liver, breast, lung and skin **(Infante-Rivard and Weichenthal, 2007)**.

2.3 Presence of isoproturon in the environment

The commercial substances containing isoproturon exist in liquid and solid formulations. Pollution of the environment with isoproturon may originate from industrial release during the manufacturing processes (point contamination). It can also result from agricultural use (diffused contamination) and as a result of point contamination in farmyards. However, point contamination was reported to represent less than 2% of the overall contamination **(INERIS, 2007)**, thus, indicating that agricultural use represents the main IPU source into the environment.

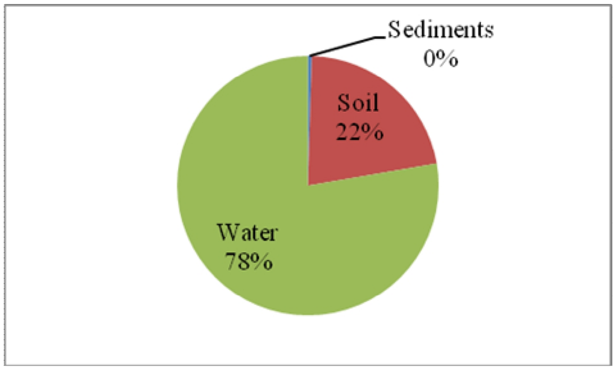


Figure 6. Distribution of isoproturon in different compartments of environment (Tissier et al., 2005)

Due to low vapour pressure, isoproturon is very rarely found in the air **(Tissier et al., 2005)**. Isoproturon has a very low tendency to adsorb on the soils and sediments, and is considered as a moderately mobile substance **(INERIS, 2007)**. This is confirmed by the PBT profiler (www.pbtprofiler.net) which has been recommended by the EPA (USA) to estimate the fate of pesticides in different compartments of the atmosphere. PBT profiler suggests that IPU is mainly found in the soil (86%) and water (13%) but negligible in air and sediments (Figure 6). However, several studies suggest that it is predominantly found in the water compartments. Isoproturon is often detected in surface and ground waters in Europe at levels exceeding the European Union drinking water limit fixed to 0.1 μgL^{-1} **(Nitchke and Schussler, 1998)**. According to a report of IFEN it was found in 87% of the surface and 86% of the ground water samples tested in France **(IFEN, 2007)**. The importance of the contamination of water resources with IPU depends on environmental factors such as rainfall (intensity and timing) and on physicochemical properties. High solubility of isoproturon in water and its stability at high range of pH values contribute to its persistence in the soil environment and favour its transfer to water resources. As a consequence, IPU is relatively recalcitrant in the environment being degraded up to 40% three months after its application **(Harris et al., 1994)**. It has also been included in a list of hazardous substances compiled by European Commission in 2001**(European Commission, 2001).**

2.4 Degradation and mineralization of isoproturon

IPU is stable against chemical degradation in aqueous solution at moderate temperatures and at pH values varying between 4 and 10 **(Gerecke et al., 2002)**. As a consequence, chemical degradation of IPU is often considered very low in most of the agricultural soils. However, under the action of UV radiation, IPU can be photo chemically decomposed in the water as well as in the first millimeters of soil leading to its transformation to monodemethyl isoproturon (MDIPU) and then to didemethyl isoproturon (DDIPU)**.** The photodecomposition of IPU in aqueous medium can reach up to 50% of the initially added product in about 70 days. This reaction can also be realized and detected on soil surface. Recent studies described the enhanced photocatalytic degradation of isoproturon and of its main metabolites by solar light in the aqueous systems in the presence of some catalysts **(Sharma et al., 2008a).** In addition, IPU is degraded by ozonation in aqueous solution forming different types of intermediate and final by-products **(Mascolo et al., 2001)**.

2.5 Treatment technologies

Traditionally, herbicides in water are removed using granular or powdered activated carbon, nano filtration, 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. 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 (8) **(Haber and Weiss, 1934**).

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \qquad (8)$$

The oxidation using Fenton‘s reagent has proven a promising and attractive treatment method for the effective decolonization and degradation of dyes (**Wang 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 et al., 2004**).

2.6 Fenton and Photo-Fenton reaction

The reaction between dissolved iron and H_2O_2 was first described by Fentonin, 1894 (**Benatti 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 the ferric ion, Fe^{3+} exists below pH 3, $Fe(OH)^{2+}$ 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, neutralization, and coagulation and precipitation **(Bautista et al., 2007).** There are many different ways to produce $HO^{\bullet}$, among which the photo-Fenton process has shown to be the most efficient one for pesticide-containing wastewater treatment **(Maldonado et al., 2007)**, achieving higher reaction yields with lower treatment costs, mainly due to a more efficient use of solar light as photon source. The need to remove residual dissolved iron and the problem related to sludge disposal have been pointed out by (**Bautista et al., 2007).**

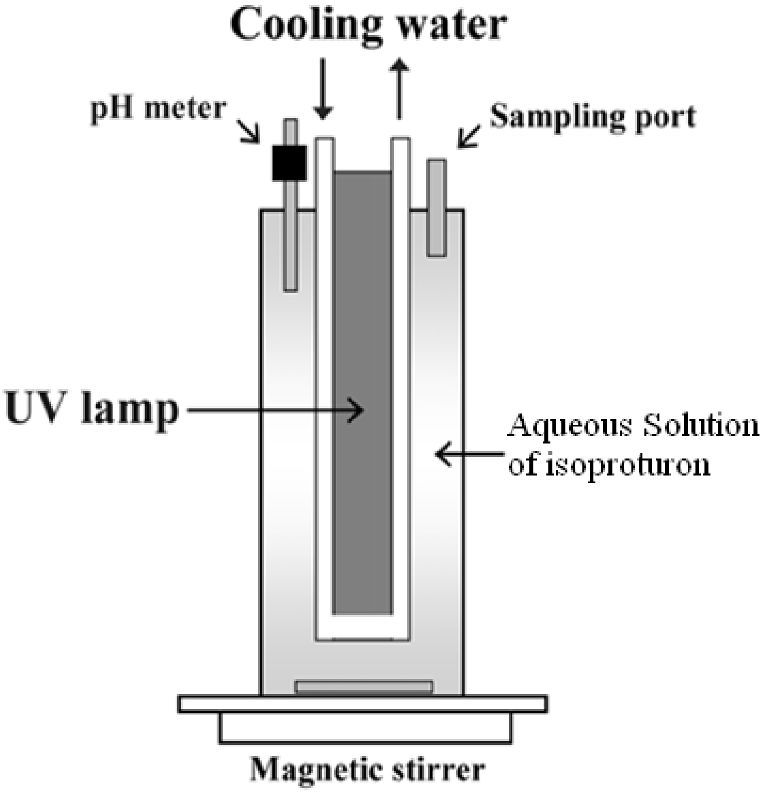


Figure 7. Schematic diagram of reactor for the Fenton and photo-Fenton process (Seong-Hoon Hong et al., 2008)

Degradation products of atrazine were identified by HPLC after application of the Fenton reaction and modified Fenton reaction. Atrazine was gradually dissolved, and two different degradation pathways were suggested. Results show that both Fenton and Fenton-like reactions are able to degrade atrazine to toxicologically inactive small organic molecules such as oxalic acid, urea, formic acid, acetic acid, and acetone, or are able to mineralize atrazine to form CO_2 and H_2O.

2.7 Homogenous Fenton reaction

The Fenton reaction has its own unique advantage in the degradation of pollutants as one of advanced oxidation processes (AOPs) because its reagents are environmentally benign, cheap and relatively easy to obtain and handle. Homogeneous systems generally offer effective contaminant removal at high rates **(Kwon et al., 1999).**The metal catalyst added as soluble salt however, dissolves in water and cannot be retained in the process. The traditional homogeneous Fenton reaction works only in the pH range of 2.0–4.0 and tends to be highest at around pH 3.0 and then decreased with increasing pH, for example, the Fenton process nearly comes to halt as the pH increases from 3.0 to 7.0 when p-hydroxybenzoic acid was degraded in the system of homogenous Fenton **(Rivas et al., 2001).**

However, iron ions which act as catalyst are dissolved in water in the homogeneous Fenton process**.** Remained iron ions in the treated water normally exceed 10 mg/L and need to be removed. This adds to the cost as well as secondary pollution, thus limiting its industrial application. To overcome such limitations and to synthesize reusable catalysts, efforts have been made to develop hetero-Fenton catalysts, such as Fe-treated laponite**,** iron exchanged zeolite **(Tekbas et al., 2008)** and iron-loaded resin **(Cheng et al., 2007).** Many researchers have reported that pillared clays intercalated by iron cations have been used as active heterogeneous Fenton catalyst in decolouration and mineralization of azo dyes. For example, **(Feng et al., 2003)** developed a laponite clay-based Fe nanocomposite as a photo-Fenton catalyst, which exhibited high photocatalytic activity for the degradation of azo dye Orange II in the presence of UV irradiation and H_2O_2.

2.8 Heterogeneous Fenton reaction

Heterogeneous catalysis offers significant advantages in separation since in this case; the catalyst can be easily recovered by sedimentation or filtration and further used. Different types of solids can be used as heterogeneous catalysts. Among them iron powder and different iron oxides have been tested **(Lucking et al., 1998).**Solid catalysts can also be constituted by iron dispersed on different supports such as alumina**,** zeolite **(Fajerwerg et al., 1996; Centi et al., 2000) ,** cation exchange resins and clay **(Barrault et al., 2000).** The catalytic activity can be related to the activation of hydrogen peroxide by iron ions leached from the solid material and acting as homogeneous catalysts **(Lucking et al., 1998; Titus et al., 2004).**

The main advantage in comparison with homogeneous catalysis is the slow release of metal ions that limits undesired reactions. Other authors **(Fajerwerg et al., 1996)** associated the catalytic activity to the combined and pH dependent effects of metal leaching and direct heterogeneous catalysis. In the latter case, the initiation step involves H_2O_2 adsorbed on the iron oxide surface **(Kwan et al., 2003)**.

2.9 Various heterogeneous catalysts

ICW (iron containing waste) is rich in iron and can be used as a catalyst in heterogeneous Fenton process for wastewater treatment. The use of ICW as heterogeneous Fenton catalyst may give numerous advantages over the classic heterogeneous/homogenous Fenton catalysts. In case of comparison with homogeneous Fenton catalysts, these advantages are less sludge production and easy separation of the catalyst **(Bautista et al., 2008)**. However, it is a cost-effective catalyst when compared with other heterogeneous Fenton catalysts such as Fe_2O_3, S-doped Fe_2O_3, and Fe_3O_4 **(Feng et al., 2004).**

Potential of coal fly ash as a heterogeneous catalyst-

Fly ash, a solid waste of coal-fired thermal power plants, contains a number of metallic and nonmetallic 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 et al., 1998).**

Most of the above 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, 1992).**

Thus, fly ash seems to be an active heterogeneous catalyst for H_2O_2-based oxidative degradation of hazardous effluents. 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.

Moreover the catalyst was of great importance for application due to its good stability, easy physical solid–liquor separation, little irons leaching and no need to be regenerated**.** The mixed substrates of modified fly ash and TiO_2 proved to be highly efficient in cadmium adsorption, even after 30 min of contact, and methyl-orange could be well removed, with efficiencies above 75% (after 300 min), when H_2O_2 was added to systems with the dye concentration of 0.05 mM. Wastewaters containing mixed cadmium–methyl-orange can be treated using modified fly ash and photo-Fenton systems, under UV irradiation **(Visa et al., 2013).**

Use of EAF dust as a heterogeneous catalyst-

Electric arc furnace (EAF) dusts are an industrial by-product, which could be an interesting heterogeneous catalyst. These dusts are recovered in gas cleaning units during the production of steel in electric arc furnaces, which are fed with scrap metal. EAF dust composition can vary greatly depending on the scrap metal composition, furnace additives, operating conditions, degree of recycling of dusts in the steelmaking process and on the type of steel produced. The high temperature of the EAF process results in the volatilization of iron and zinc, which is predominantly used as a corrosion inhibiting coating on steel products.

Chemical oxidation tests using H_2O_2 were performed on a solution contaminated with 100 mgL^{-1} of pentachlorophenol (PCP). The effectiveness of electric arc furnace dust and hematite as heterogeneous catalysts was evaluated. Reactions were conducted at pH 2 for 24 h. Results showed that the maximum removal yields for electric arc furnace (EAF) dust were achieved.

EAF dust was responsible for chloride ion and zinc release in the solution and this must be taken into account in developing the process **(Mecozzi et al., 2006).**

Steel dust used as heterogeneous catalyst-

Steel dust is also used as heterogeneous catalyst for Fenton-like oxidation of polychlorinated dibenzo-*p*-dioxins (PCDD). The steel dust was treated using a chemical acid etchant (HCl) and ultrasound to remove surface anchored groups, reduce aggregation, and thereby increase the specific surface areas, resulting in increased access to catalytic sites. When a PCDD mixture was treated, steel dust achieved 88% removal. These results indicate that the steel dust is a potentially viable catalyst for removing PCDDs from contaminated water **(Lee et al., 2009).**

Efficiency of natural clay as heterogeneous Fenton and photo-Fenton catalyst-

The use of clays as catalysts for Fenton-like reactions is therefore a promising alternative for decontamination of soils, groundwater, sediments, and industrial effluents because they are natural, abundant, inexpensive, and environmentally friendly **(Ramirez et al., 2010).** To avoid all the disadvantages of catalysts synthesis, natural containing Fe-clay could be an interesting alternative as heterogeneous catalyst.

A total phenol conversion and a 70% total organic carbon (TOC) removal were obtained within a period of 6 h at ambient temperature, atmospheric pressure and low concentration of hydrogen peroxide by Fenton oxidation using sieved and calcined Fe-clay. A total phenol and tyrosol conversion was also obtained in less than 20 min by photo-Fenton-like oxidation. The high stability of the clay in the reaction condition and its good catalytic performance in pollutant conversion and TOC abatement showed great promise for the treatment of organic pollutant in wastewater **(Djeffal et al., 2013).**

Heterogeneous Catalytic performances of a Fe-exchanged Al-pillared synthetic beidellite-

Recently, transition metal exchanged zeolites **(Fajerwerg et al., 1996; Centi et al., 2000),** Cu_2 containing montmorillonites and Fe_3 containing pillared montmorillonites have been proposed as active catalysts for organic compounds oxidation. In contrast to previous studies, using iron ions supported on alumina, these authors concluded that it was possible to develop a stable heterogeneous catalyst, combining the efficiency of homogeneous processes, i.e. Fenton type and the advantages of heterogeneously-catalyzed processes. These catalysts show a higher rate of conversion of the pollutant, as well as a lower sensitivity to pH than iron ions in solution, at the same reaction conditions. In addition, some of these catalysts exhibit marginal leaching of the cations, keeping their activity during successive runs **(Barrault et al., 2000).**

At pH 5.0, the Fe-exchanged Al-pillared synthetic beidellite allows the total elimination of phenol and a significant COD removal, without generating additional pollution by iron hydroxide sludge’s. In addition, the catalyst can be reused for successive runs, without significant loss of activity **(Cezar Catrinescu et al., 2003)**.

Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst-

Vermiculite is a clay mineral which is composed of octahedral alumina or magnesia sandwiched between two tetrahedral silicate sheets**.** Being low cost and widely available, vermiculite has been exploited widely over the past 50 years or more and used for the adsorption of heavy metal ions **(Alvarez-Ayuso et al., 2003),** oils **(Mysore et al., 2005)** and pesticides **(Abate et al., 2005).** Reactive Brilliant Orange X-GN in an aqueous solution could be effectively degraded by a heterogeneous photo-Fenton process with Fe-VT as catalyst. Leaching tests found that an amount of iron ions was less than 1ppm in aqueous solution. Due to its favorable photo catalytic properties and excellent long-term stability, iron pillared vermiculite is a promising catalyst for dyeing wastewater treatment **(Chen et al., 2010).**

2.10 Based on the exhaustive analysis of the existing literature on the application of Fenton oxidation to wastewater treatment, following optimum conditions is outlined-

Operating pH

Fenton process is strongly dependent on the solution pH mainly due to iron and hydrogen peroxide speciation factors. The optimum pH for the Fenton reaction was found to be around 3, regardless of the target substrate **(Rivas et al., 2001).**

The activity of Fenton reagent is reduced at higher pH due to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate **(Parsons, 2004).** At very low pH values, iron complex species exist, which reacts more slowly with hydrogen peroxide than other species **(Xu et al., 2009).** Therefore, the efficiency of the Fenton process to degrade organic compounds is reduced both at high and low pH. Thus an adequate control of pH would increase process efficiency. It should be noted that the type of buffer solution used also has effect on the degradation process **(Benitez et al., 2001).**

Amount of ferrous ions

Usually the rate of degradation increases with an increase in the concentration of ferrous ion **(Lin et al., 1997)**. However, the extent of increase is sometimes observed to be marginal above a certain concentration of ferrous ion as reported by **(Rivas et al., 2001).** Also, an enormous increase in the ferrous ions will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the total dissolved solids content of the effluent stream and this is not permitted.

Hydrogen peroxide concentration

Concentration of hydrogen peroxide plays a more crucial role in deciding the overall efficiency of the degradation process. Usually it has been observed that the percent degradation of the pollutant increases with an increase in the dosage of hydrogen peroxide **(Lin et al., 1997)**. However, care should be taken while selecting the operating oxidant dosage. The unused portion of hydrogen peroxide during the Fenton process contributes to COD **(Lin et al., 1997)** and hence excess amount is not recommended. Thus, the dosage of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized and this can be decided based on the laboratory scale studies.

Initial concentration of pollutant

Usually lower initial concentrations of the pollutants are favoured **(Benitez et al., 2001)**, but then negative effects of treating large quantity of effluent needs to be analyzed before the dilution ratio is fixed. For real industrial wastewater, dilution is essential before any degradation is effected by Fenton oxidation.

Based upon thorough literature survey, although considerable search have been done on photo-Fenton for degradation but very rare studies have been done using foundry sand as iron source for degradation of pesticide. Advanced oxidation processes (AOP's) appear to be a promising field of study, which have been reported to be effective for the degradation of soluble organic contaminants in waters and soils. But high cost of AOP's renders its application in waste water treatment. On the other hand, the existing conventional methods are not efficient to treat toxic, non-biodegradable organic pollutants, and new improved treatment methods have to be developed and tested. Based on the literature survey, most of the studies have been done using homogenous catalyst for degradation of organic contaminants but this add other pollutants to the water and also produce iron sludge thus again posing threat to safe disposal of water treated and iron sludge produced. Thus, it is need of the hour to seek for cheap and readily available alternative iron source. A considerable number of studies have been reported on the physical characteristic of foundry sand (FS), very little attention has been paid to its catalytic activity.

Chapter 3

Materials and methods

3.1 Reagents and chemicals

Isoproturon (IPU), N,N-dimethyl-N'-[4-(1-methylethyl)phenyl] urea (Figure 8), Technical grade (95%), was obtained from Pioneer Pesticides Pvt. Ltd, Chandigarh (India) and used as such without any further purification. Waste Foundry sand was received as a gift sample from local industry and used as such as received without any further modifications. H_2O_2 (30% w/v) was purchased from SD Fine Chemicals Limited, India. 0.1 N H_2SO_4 was used for adjusting the pH of IPU solution. All the chemicals were of analytical grade and used as such without any further purification throughout the study. For the experimental study 25 mgL^{-1} IPU solution was used. For the preparation of all the solutions double distilled water was used.

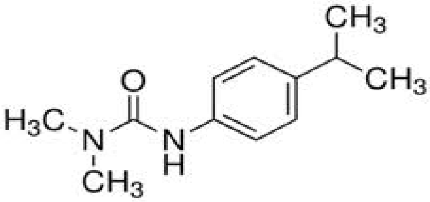


Figure 8. Structure of isoproturon

3.2 Instruments used

pH meter: pH of the solution was monitored by using a digital desktop, pH meter and pH was adjusted with the help of 0.1 N NaOH and 0.1 N H_2SO_4. 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 at 239nm.

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 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.

3.3 Photoreactors: In our study, we have worked upon two type batch reactor one was shallow pond batch slurry reactor and other was solar baffled batch reactor (SBBR) with recirculation.

Shallow pond batch slurry reactor: The shallow pond batch slurry reactor as shown in Figure 9(a) was made up of borosil glass, 16 cm in diameter and 5.2 cm in height with a capacity of 1200 mL. For heterogeneous solar photo-Fenton studies, 200 mL of IPU solution (25 mgL^{-1}) was taken in this reactor at pH 3 and known amount of Fenton reagent ($FS+H_2O_2$) was added. Samples were taken after regular intervals and analyzed for degradation studies.

Solar baffled batch reactor with recirculation: The experiments were also performed using solar baffled batch reactor with recirculation as shown in Figure 9(b), was made up of concrete (20 x 30 cm) with four equally spaced baffles. The baffles were made up of cast iron fitted in batch reactor to increase the retention time of the solution to be treated. The base of the reactor was covered with plastic sheet as concrete will increase the pH of solution which ultimately stops Fenton reaction.

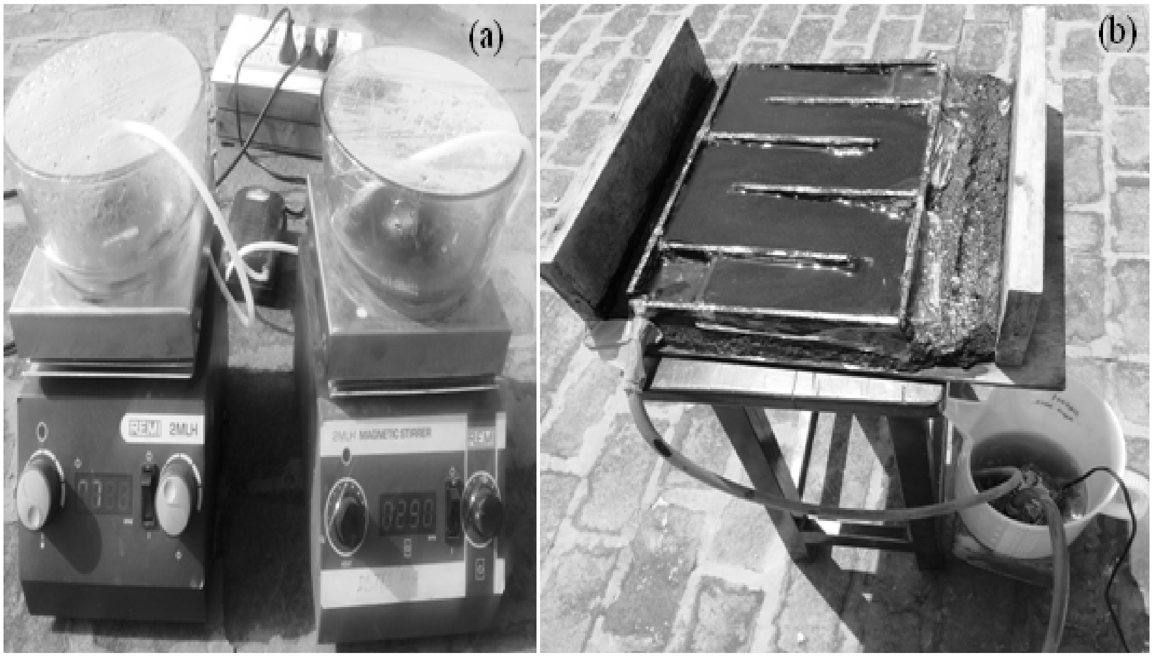


Figure 9. Illustration of the (a) Shallow pond batch slurry reactor and (b) SBBR with recirculation for the degradation of IPU.

3.4 Analytical analysis

The degradation studies were performed with UV- visible Spectrophotometer (Hitachi V- 500 UV/VIS (Japan)) double- beam spectrophotometer with isoproturon (IPU) having λ_{max} at 239 nm.

For characterization of foundry sand (FS), scanning electron microscope (SEM) was used. Energy-dispersive X-ray spectroscopy (EDS) was performed for foundry sand to determine its chemical composition using same instrument. The analysis showed absence of any heavy metals which is susceptible to leaching simultaneously showed good percentage of iron (23%) required for photo-Fenton studies.

3.5 Preparation of solution

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 was 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 mgL^{-1} concentration were prepared by dissolving 25 mg isoproturon in double distilled water and make the solution quantity to 1 L.

3.6 Experimental Procedure

Solar Photo-Fenton: IPU solution of 25 mgL^{-1} was prepared by double distilled water. 200 mL of sample taken in shallow pond batch slurry reactor, known amount of FS and known amount 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 regular intervals of 30 min 180 min and filtered from 0.45 micron syringe filter. The concentrations of these samples were detected by Spectrophotometer.

Solar baffled batch reactor with recirculation: The experimental condition was same as in above , the only difference was experiment was carried out in solar baffled batch reactor with recirculation. The baffles were made up of cast iron fitted in batch reactor to increase the retention time of the solution to be treated. The base of the reactor was covered with plastic sheet as concrete will increase the pH of solution which ultimately stops Fenton reaction.

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 regular intervals of 30 min for 180 min. The concentration of these samples were detected by Spectrophotometer.

Leaching Experiment: In our studies, leaching experiment was carried out by adding appropriate amount of foundry sand into 200 mL of isoproturon solution using stirring overnight. After filtration through blotting sheet, the reaction was started by adding optimized H_2O_2 at pH 3. Air was also supplied by the aerator during experiment. Set up was placed in sunlight. Sample was taken in regular intervals of 30 min 180 min. The concentrations of these samples were detected by Spectrophotometer.

All the solar experiments were carried during timings 10.00 A.M. to 3.30 P.M. in months of March to May, 2014 at Patiala, Punjab. Experiments were repeated thrice to check the reproducibility of results and average values are reported.

Chapter 4

Results 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 having λ_{max} at 239 nm.

4.1 Standard curve of isoproturon

Standard curve for isoproturon is prepared by plotting the graph between varying known concentration ranging from 0 mgL^{-1} to 30 mgL^{-1} and its absorbance at 239 (Figure 10). From this graph we can calculate unknown concentration for solution. Value of R^2 is 0.998 and slope is 0.051.

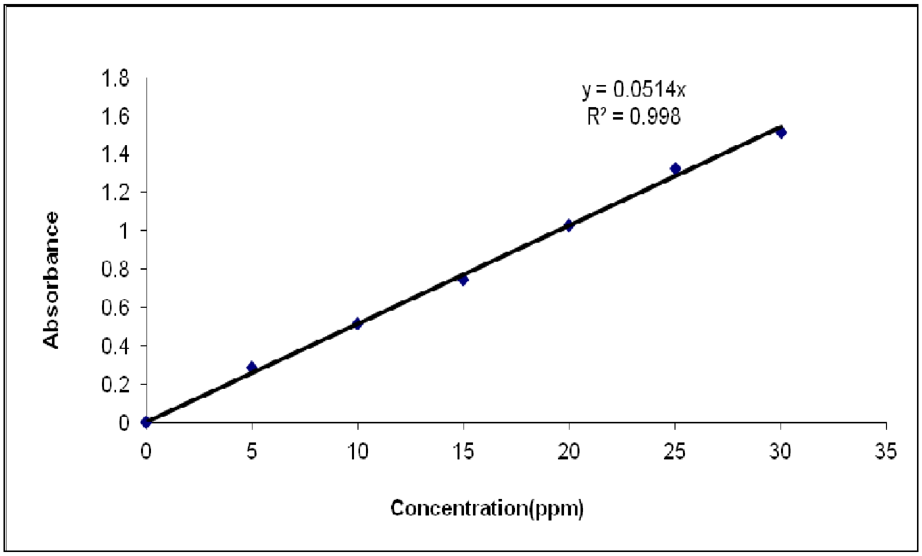


Figure 10. Standard curve of isoproturon (IPU)

4.2 Characterization of Foundry sand (FS)

Characterization of foundry sand (FS) was done using scanning electron microscope (SEM) and results was shown in Figure 11 (a). Energy-dispersive X-ray spectroscopy (EDS) was performed for foundry sand to determine its chemical composition using same instrument Figure 11 (b) which is reported in Table 2. The analysis showed absence of any heavy metals which is susceptible to leaching simultaneously showed good percentage of iron (23%) required for photo-Fenton studies.

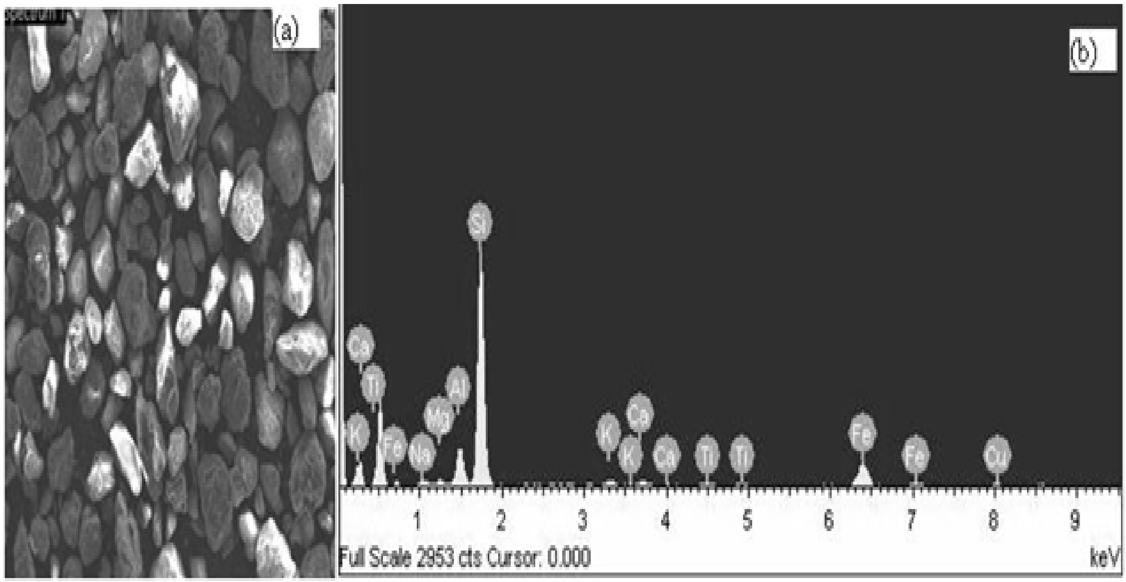


Figure 11. (a) SEM micrograph of FS (b) EDS pattern of FS.

Table 2. Mean composition of foundry sand used in study

Element	Na K	Mg K	Al K	Si K	K K	Ca K	Ti K	Fe K	Cu K	Total
Weight%	1.93	1.21	7.85	58.10	1.77	1.49	1.36	23.16	3.13	100

4.3 pH monitoring experiments

One of the major limitations of using different heterogeneous catalyst in photo-Fenton studies is variation in pH during the reaction. Normally the pH of the solution increases with time after addition of heterogeneous catalyst, which ultimately stops Fenton reaction **(Mecozzi et al., 2006)**. In this context, the change in pH studies with time has been performed using different amount of foundry sand. The initial pH was adjusted at pH 2 and was continuously monitored for 240 min after addition of different foundry sand concentration. There was no significant change in the pH even after 240 min (Figure 12). This eliminates the necessity of continuous pH adjustment i.e. in the range of 2-3 pH for photo-Fenton studies.

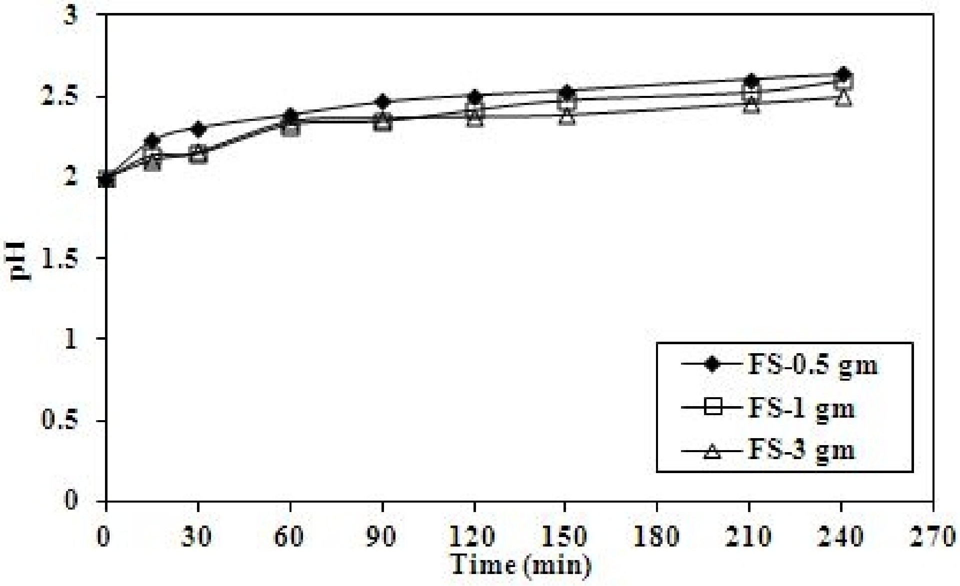


Figure 12. pH variation experiments with time for different doses of FS

4.4 Preliminary experiments

Before the detail investigation regarding the heterogeneous Fenton catalytic activity of foundry sand on the herbicide degradation, different preliminary experiments were performed to evaluate the benefit and efficiency of each condition. Preliminary experiments were carried out as follows:

(1) Sunlight only (2) FS only (3) H_2O_2 only (4) H_2O_2 +sunlight (5) FS + sunlight (6) FS+ H_2O_2 (7) FS + H_2O_2 +sunlight

Sunlight alone was not efficient process since less than 25 % degradation of isoproturon within 180 min was observed. Negligible degradation (4.16%) was achieved with foundry sand only in 180 min thus confirming negligible adsorption. From the results it was observed that herbicide was resistant to the oxidation from H_2O_2 alone (Figure 13). The combined action of H_2O_2 and sunlight lead to 64.4% degradation in 180 min. Less than 20 % degradation in 180 min was achieved with combination of foundry sand and sunlight. In Fenton process (FS+ H_2O_2), around 8% degradation was achieved in 180 min. Maximum degradation efficiency 97 % was observed in solar photo-Fenton process (FS+ H_2O_2 + sunlight).

The relative efficiencies of the above combinations are in following order:

FS + H_2O_2 +sunlight> H_2O_2 +sunlight> sunlight only > FS + sunlight> FS + H_2O_2 > H_2O_2 only> FS only.

Thus from the studies, it was confirmed for getting higher degradation efficiency solar photo-Fenton came out to be best treatment for isoproturon.

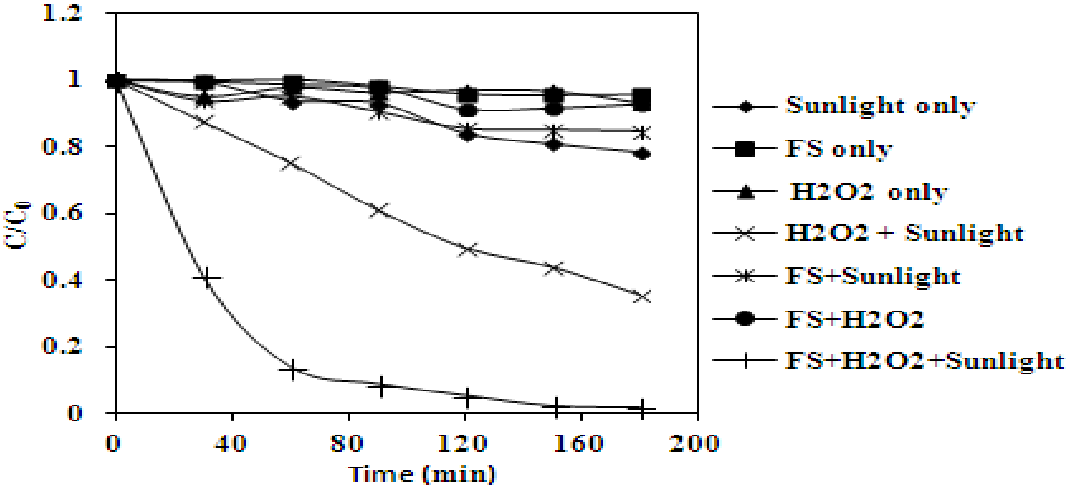


Figure 13. Result of different preliminary experiments to evaluate the benefit and efficiency of each condition.

4.5 Effect of H_2O_2 concentration

For completing any Fenton reaction stoichiometry amount of H_2O_2 is very important. Amount less or more than stoichiometry amount of H_2O_2 generally leads to lesser degradation rates. With excessive H_2O_2, it can react with OH radicals and inhibit Fenton reaction (9).

$$H_2O_2 + OH^{\bullet} \longrightarrow H_2O + HO_2^{\bullet} \tag{9}$$

The excess amount also reacts with ferric ions yielding Fe (III) - hydroperoxy **(Guimarães et al., 2014)**, thus reducing the number of ferrous ions required for Fenton reaction. Ferric ions reduced to ferrous ions in the presence of iron i.e. Fenton reaction. In this view, H_2O_2 was varied from 0.0 mM to 13.2 mM for degradation of isoproturon by keeping the other operating condition fixed (pH 3, $C_0 = 25$ mgL^{-1}, and FS = 2 gm). The initial increase of H_2O_2 concentration up to 2.2 mM lead to increase in degradation rate to 90% after 90 min as expected because more OH radicals will be formed. The removal efficiency was almost constant till 6.6 mM, decreased thereafter as H_2O_2 concentration was increased from 6.6 mM to 13.2 mM as shown in figure 14. Thus, the H_2O_2 concentration 2.2 mM was used for further experiments.

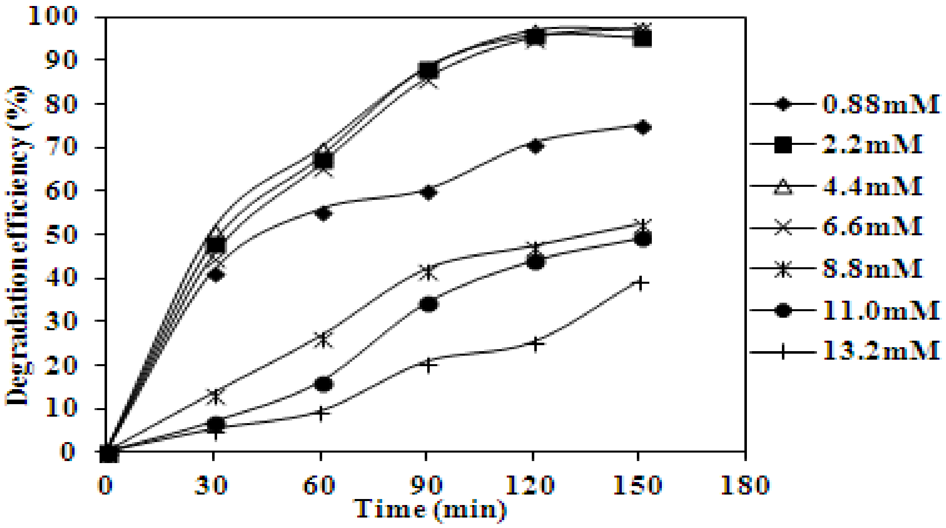


Figure 14. Effect of initial H_2O_2 concentration on IPU degradation during photo-Fenton process (pH 3, $C_0 = 25$ mgL^{-1}, and FS = 2 gm).

4.6 Effect of foundry sand concentration

The effect of foundry sand concentration on degradation of isoproturon is shown in figure 15. Foundry sand concentration was varied in the range of 0.25-3.5 gm while keeping other operating condition unchanged i.e. pH 3, H_2O_2=2.2 mM and C_0 = 25 mgL^{-1}. The herbicide degradation increased with increasing foundry sand concentration. The 86% degradation of herbicide was achieved with foundry sand concentration of 0.5 gm after 60 min. On the other hand, increasing foundry sand above 0.5 gm may inhibit the process efficiency due to the scavenging of hydroxyl radical (10) **(Yang et al., 2013).**

$$OH^{\bullet} + Fe^{2+} \longrightarrow OH^{-} + Fe^{3+} \qquad (10)$$

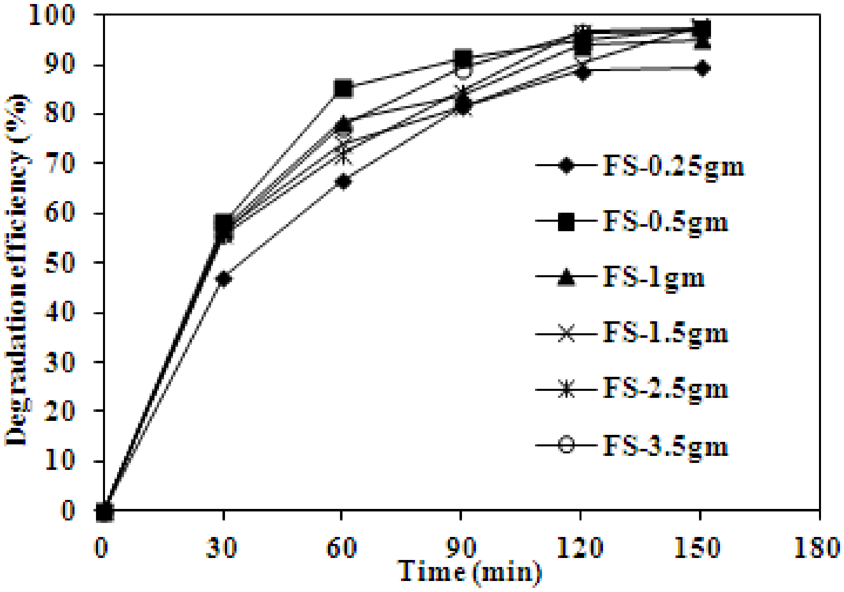


Figure 15. Effect of FS dose on IPU degradation during photo-Fenton process (pH 3, H_2O_2=2.2 mM and C_0 = 25 mgL^{-1}).

4.7 Effect of IPU concentration

The effect of initial IPU concentration on the photo-Fenton process was observed, since pollutant concentration is an important parameter in wastewater treatment keeping other operating conditions fixed at pH 3, FS= 0.5 gm and H_2O_2 = 2.2 mM. As shown in Figure 16, the efficiency of degradation increased with the increase in the pesticide concentration. The increase of pesticide concentration from 5 to 25 mgL^{-1} increased the degradation efficiency from 88% to 97% after 150 min. A higher concentration increases the number of IPU molecules per volume unit, increases the probability of collision between isoproturon molecule and oxidizing species, which lead to enhancement in the degradation efficiency **(Daud & Hameed, 2010).**

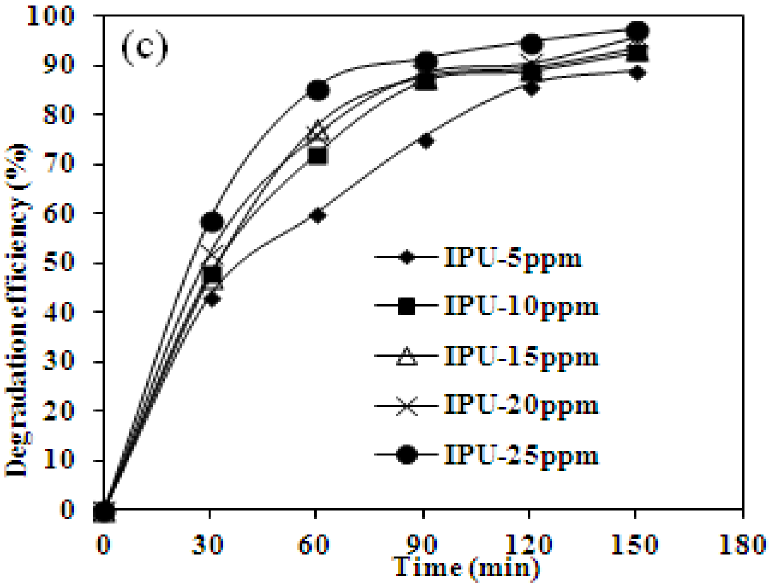


Figure 16. Effect of IPU concentration on IPU degradation during photo-Fenton process (pH 3, FS= 0.5 gm and H_2O_2 = 2.2 mM).

4.8 Effect of pH

Figure 17 illustrates the effect of pH on the IPU degradation using FS as heterogeneous catalyst. The experiments were carried out at pH range of 2-7 keeping other operating conditions fixed at FS= 0.5 gm and H_2O_2 = 2.2 mM. It was observed that maximum degradation efficiency (97.32%) was found at pH 3. However, further increasing pH from 3 to 7 resulted in decreased degradation efficiency (35.21%). The reduction in efficiency at high pH value might be due to the precipitation of iron as $Fe(OH)_3$ thereby lowering its ability to catalyze H_2O_2 **(Saritha et al., 2007)** and lower the transmission of the radiation **(Saritha et al., 2007)**. Secondly, the decrease in degradation efficiency might be due to the dissociation and auto-decomposition of H_2O_2 **(Tamimi et al., 2008)**. It was also known that there was decrease in the oxidation potential of OH radical with increasing pH **(Tamimi et al., 2008)**. The slight reduction in degradation efficiency at pH lower than 3 was due to OH radical scavenging of H^+ ions (11) **(Tamimi et al., 2008).**

$$OH^{\bullet} + H^+ + e^- \longrightarrow H_2O \qquad (11)$$

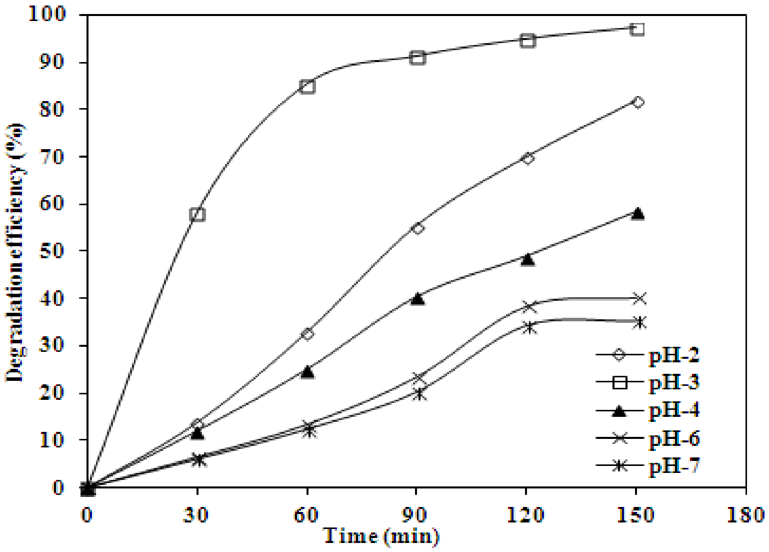


Figure 17. Effect of pH on IPU degradation during photo-Fenton process (C_0 = 25 mgL^{-1} FS= 0.5 gm and H_2O_2 = 2.2 mM).

4.9 FS recycling studies

For the field applications of heterogeneous solar photo-Fenton, the stability of the catalyst is very important. In this regard, the catalytic activity of the foundry sand for subsequent cycles for degradation of isoproturon i.e. Recycling studies were conducted. After completion of each run, foundry sand was separated from solution by filtration and then washed with distilled water, dried at 80^0C for 1h and was reused for next run with fresh isoproturon solution. The foundry sand was effectively recycled for four times with 20% reduction in degradation efficiency. The morphology of recycled FS was unchanged as clear from SEM-EDS (Figure 18 (a) and (b)). The reduction in efficiency of catalyst might be due to accumulation of intermediates formed during oxidation, surface deposition and loss of active phase leaching **(Daud & Hameed, 2010).** This reduction in degradation efficiency might also be due to some loss in weight of FS during filtration (nearly 5%) as clear from figure 18(c). Leachate after every cycle was tested for the total dissolved iron concentration and in every case it was found less than 3 mgL^{-1} i.e. the discharge limit (EPA, 1986).

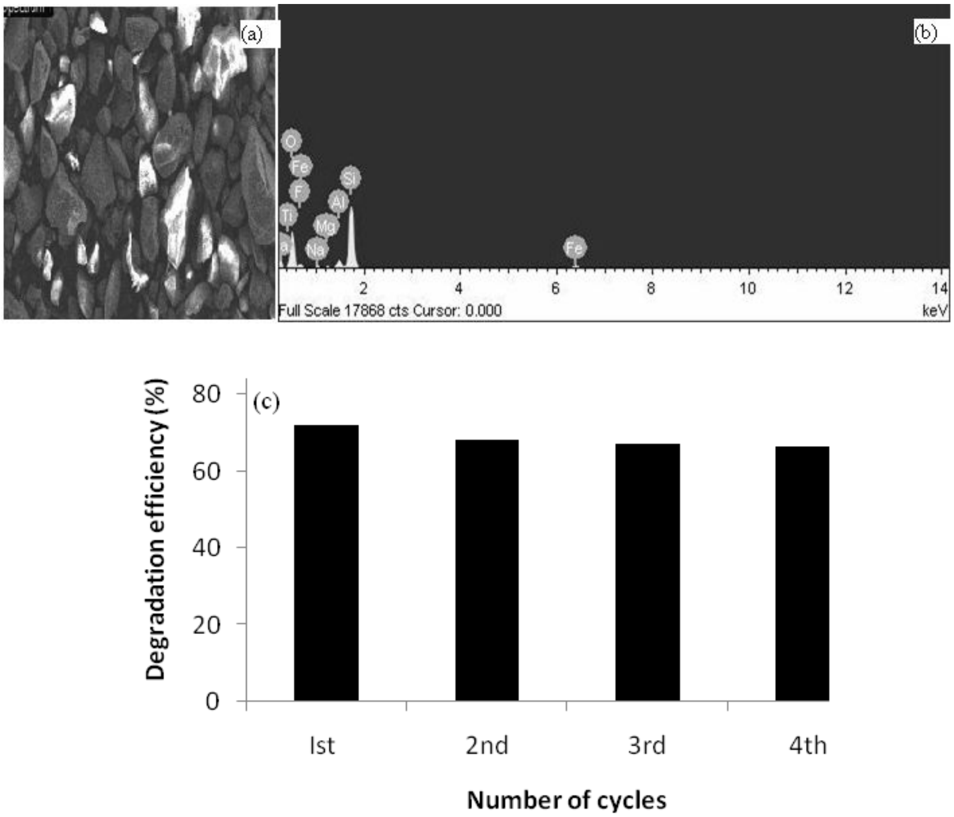


Figure 18. (a) SEM micrograph (b) EDS pattern (c) Results of recycled FS.

4.10 Effect of area/volume (A/V) ratio

For field scale applications of solar photo-Fenton process using foundry sand as catalyst, the depth of reactor is very important. Generally for more solar light penetration, less depth and more area is recommended. This can be achieved by both keeping the volume constant and area varied or by keeping area constant and volume varied. In our studies, we varied the volume by keeping the aperture constant. In this view, A/V variations of slurry pond reactor were varied from 0.76 to 5.35 cm^2mL^{-1}. The degradation efficiency increased with the reduction in the volume of the sample to be treated i.e. less depth (Figure 19). Actually, reducing the volume increases A/V ratio thus enhancing surface area of solution leading to increase in path length of photons resulting in more OH radicals **(Verma et al., 2013)**.

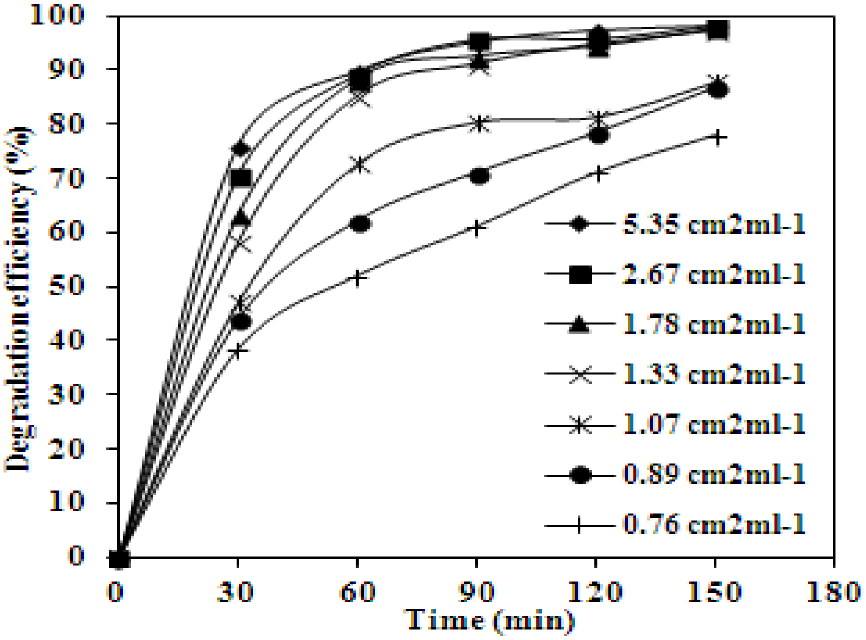


Figure 19. Effect of A/V ratio on IPU degradation during photo-Fenton process (C_0 = 25 mgL^{-1}, pH 3, FS= 0.5 gm and H_2O_2 = 2.2 mM).

4.11 Effect of iron leaching

Generally, in photo-Fenton studies, handling of iron sludge adds other pollutants to the water which can pose threat to environment. In this view, efforts have been done to leach out iron from foundry sand in dissolved iron form to catalyze the photo-Fenton studies. In our studies, leaching experiment was carried out by adding 0.5 gm of foundry sand into 200 mL of isoproturon solution using stirring overnight. After filtration through blotting sheet, the reaction was started by adding 2.2 mM H_2O_2 at pH 3. The degradation achieved was 85% after 150 min of solar photo-Fenton (Figure 20) treatment at iron leaching concentration 2.5 mgL^{-1}.

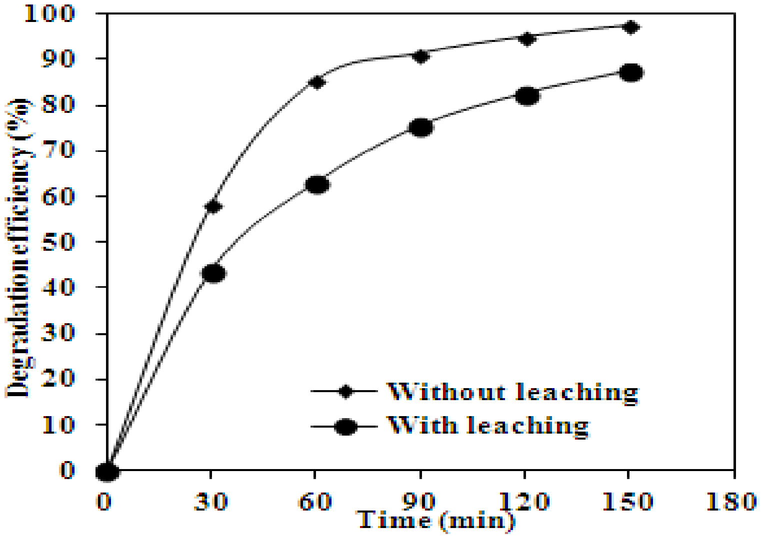


Figure 20. Effect of leach out iron from FS in dissolved iron form on IPU degradation during photo-Fenton process.

4.12 Solar Baffled batch reactor (SBBR) with recirculation

Experiment was carried out in a SBBR designed for the degradation of IPU, as shown in Figure 9(b). The optimized parameters under which the reaction was carried out were C_0 = 25 mgL^{-1} ; H_2O_2 = 2.2 mM; FS = 0.5 gm; pH 3. To limit the variation in pH during the photo-Fenton process, the bottom surface of reactor was covered with plastic and 70% degradation efficiency was achieved using this designed system after 6 h (Figure 21) with flow rate 1 $Lmin^{-1}$. Baffles were introduced into the reactor in order to increase the contact time between IPU, FS and sunlight for achieving higher degradation rates. The reactor was covered effectively for avoiding the evaporation losses. Reactors with inner layer of plastic can be a feasible alternative for the construction of reactor to limit pH variations during the reaction **(Verma et al., 2014)**.

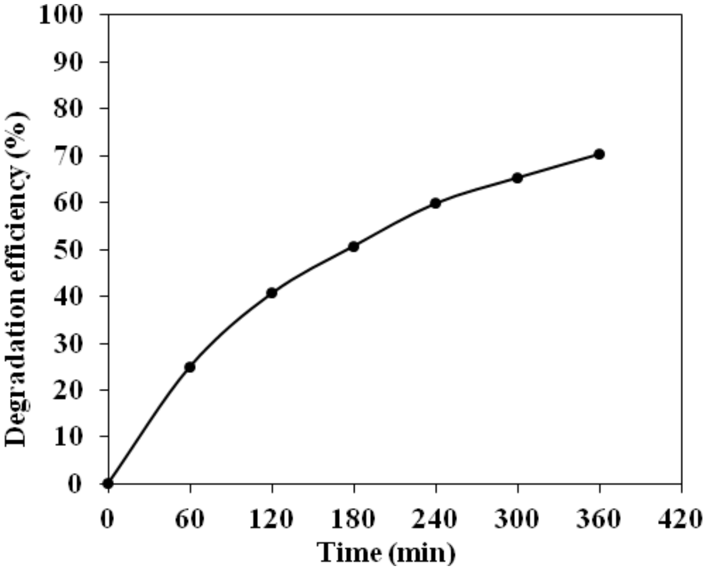


Figure 21. Result of the eexperiment was carried out in a SBBR designed for the degradation of IPU.

Chapter 5

Conclusion

In this study, we report for the first time the use FS as heterogeneous catalyst in photo-Fenton process for degradation of IPU. The effectiveness of FS as heterogeneous catalyst was evaluated and results confirmed effective use of FS as iron source in photo-Fenton degradation studies of herbicide IPU.

- The best degradation efficiency (97%) was achieved at $[H_2O_2]_0$= 2.2 mM, pH 3, FS dose=0.5 gL^{-1}, $[IPU]_0$= 25 mgL^{-1}.
- It was testified that the FS on the support surface was successfully and effectively loaded on the surface and used as catalyst in photo-Fenton process for degradation of IPU.
- 70 % degradation efficiency after 6h of treatment when subjected to 5 L capacity was achieved in SBBR with recirculation using optimized parameters. The pH of reaction remains unaltered with reactor having inner plastic lining.
- The advantages of this system are high degradation rates (97%), simple handling, environmental friendly, and low cost (waste as iron source).

This study demonstrates the utility of the solar photo-Fenton system as a treatment method either as pre or post treatment for the complete mineralization of non-biodegradable organic substances.

In fact, using foundry sand as a catalyst what is commonly considered as a waste to treat waste would be of economic interest considering the high costs required for its disposal. More retention time, durable support material, exposed area, effective supporting material for FS immobilization etc. are some of factors would be looked into for the better performance of system. With these basic efforts at lab, pilot scale and with other design modifications, the reactor can boost the commercial applications of this technology for degradation of recalcitrant compounds.

The results of the study show that photo-Fenton will be an effective, viable and economic treatment process using foundry sand for pesticide by producing higher mineralization efficiency.

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