Heterogeneous photo-Fenton degradation of dye RB5 using Fly ash and Foundry sand as iron source

A Dissertation

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Environmental Science and Technology

Submitted

By

HIMADRI RAJPUT

(Reg. No. 601201008)

Under Supervision of

Mr. Anoop Verma
(Asstt. Prof., School of Energy and Environment)

School of Energy and Environment
Thapar University, Patiala

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CERTIFICATE

This is to certify that thesis entitled, "**Heterogeneous photo-Fenton degradation of dye RB5 using Fly ash and Foundry sand as iron source**" submitted by **Ms. Himadri Rajput** 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 my supervision and guidance.

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

Mr. Anoop Verma
Assistant Professor & Supervisor
School of Energy and Environment
Thapar University
Patiala

Dr. A.S.Reddy
Head
School of Energy and Environment
Thapar University
Patiala

Dr. S. K. Mohapatra
Dean
Academic Affairs
Thapar University, Patiala

DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Heterogeneous photo-Fenton degradation of dye RB5 using Fly ash and Foundry sand as iron source**" 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.

Himadri Rajput

Himadri Rajput
(Reg. No. 601201008)
M.Tech – Environmental Science and Technology
Thapar University
Patiala

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Himadri Rajput

Chapter 1

INTRODUCTION

Our biosphere is under constant threat from continuing environmental pollution. Impact of anthropogenic activities on our atmosphere, hydrosphere and lithosphere cannot be ignored. There is negative influence over biotic and abiotic components of different natural eco-systems due to man-made activities **(Das, 2000).**

One of the most important sources of pollution in the environment is industrial effluents. Textile industrial dye effluents are significant sources in environmental pollution **(Wang et al., 2008)** as it is among one of the most water demanding sectors **(Chaco et al., 2006).** Its consumption can reach from 25 to 250 m^3 of water per ton of product, depending on the processes, the final quality of the product, the type and form of the fibres and the machinery and the equipment employed **(Comisio et al., 1998).**This water consumption, allied to high dosages of dyes, originates effluents that are extremely colorized. Most of the dyes are difficult to decolorize due to their complex structure and synthetic origin. There are more than 10,000 dyes used in textile industry and 280,000 tons of textile dyes are discharged every year worldwide **(Mass et al., 2005).**

The release of these wastewaters to natural environments is described as very problematic to aquatic life **(Chung et al., 1993)** and mutagenic to human **(Chung et al., 1992).** These dyes are the most problematic pollutants of textile wastewaters because after the reactive dyeing process is finished, more than 15% of the textile dyes is lost in wastewater stream during dyeing operation **(Park et al., 2003).** The dyes do not bind completely to the fabric and depending on the class of the dye its loss in wastewaters could vary from 2% for basic dyes to as high as 50% for reactive dyes (**Pandey et al., 2007),** causing serious environmental problems.

Unfortunately with the complicated color-causing compounds, the decolorization of these wastes is a difficult and challenging task **(Hao et al., 2000).** The removal of color from dyeing industries effluents is one of the major problems faced by the textile dyeing industry whereas from an environmental point of view, the removal of synthetic dyes has a great concern **(Hameed et al., 2007).**

Nowadays, various chemical and physical processes, such as elimination by adsorption onto activated carbon, coagulation by a chemical agent, ozone oxidation, hypochlorite oxidation, electrochemical method, etc. are applied for the treatment of dye waste effluents **(Yoshida et al., 1999; Tanaka et al., 2000; Shen et al., 2001).** Nevertheless, these methods are usually nondestructive, inefficient, costly and resulted in the production of secondary waste products. Therefore, purification of dye wastewater is becoming a matter of great concern and it is necessary to develop novel and cost-effective technologies to treat dye wastewater **(Sun et al., 2008).**

1.1 Advanced Oxidation Technologies

Advanced oxidation technologies (AOTs) shown in figure1 are innovative methods for water treatment and are extremely useful in the case of substances resistant to conventional technologies.

AOTs are oxidation processes which generate hydroxyl radicals (•OH) that are very effective in degrading organic pollutants because of their strong oxidant power and nonselective species **(Perez et al., 2002; Chan et al., 2003).** Various combinations of them are employed for the complete mineralization of pollutants.

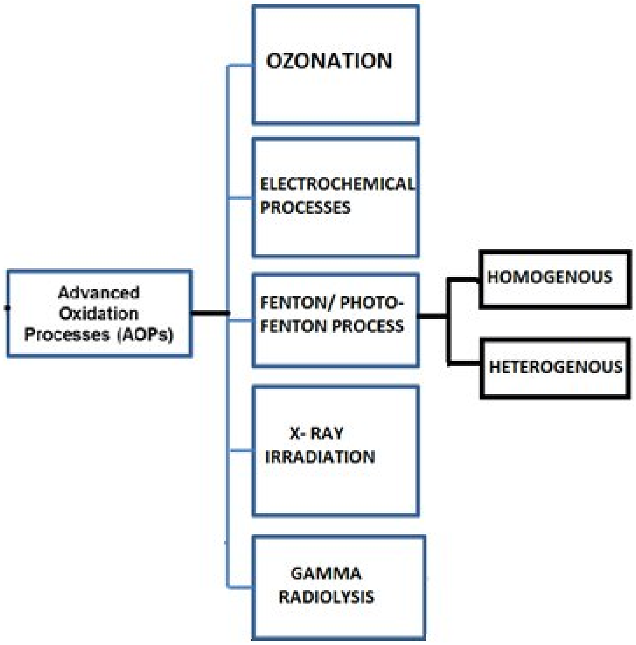


Figure1. Advanced Oxidation Process

Among these AOTs, Fenton's reagent is particularly attractive because of the low costs, the lack of toxicity of the reagents (i.e., Fe (II) and H_2O_2), and the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology **(Liao et al., 2009).**

However, it should be pointed out that the homogeneous Fenton process has a significant disadvantage i.e. sludge-containing Fe ion at the end of the wastewater and removal/treatment of which is very expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering catalyst, attempt has been made to use foundry sand and fly ash as an alternative iron source.

1.2 Foundry Sand

Foundry sand is mixture of silica sand (80–95%), bentonite clay (4–10%), carbonaceous additive (2–10%) and water (2–5%). FS is used for mould making and is high quality silica sand having uniform physical characteristics. It is a by-product of the ferrous and nonferrous metal casting industry. FS is a good source of silica, alumina, and iron oxides. Industry estimates are that annually in production approximately 100 million tons of sand is used. Of that, four to seven million tons are annually discarded and are available to be recycled into other products and industries **(American Foundry Society).** This foundry sand is black in color and contain large amount of fines. The typical physical and chemical property of WFS is dependent upon the type of metal being poured, casting process, technology employed, type of furnaces (induction, electric arc and cupola) and type of finishing process (grinding, blast cleaning and coating). In foundries industries, physical and chemical properties must be stringently met as poor quality sand can result in casting defects. Sand and foundries producers invest significant resources in quality control of their sand systems to maintain consistency. As a result, FS from an individual facility will be very consistent in composition generally, which is an advantage for most end use applications.

1.3 Fly ash

Fly ash is a waste material originating in large quantities from modern power stations. It 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 as bottom ash. In an industrial context, fly ash usually refers to ash produced during combustion of coal. 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**). Less than 10% collected is utilized in some process other than direct burial. 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.

This unproductive use of fly ash and the associated long-term financial burden of disposal and its 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 areas such as waste management, recovery of metals and agriculture has been explored (**Meunier et al., 2006**).

1.4 Model compound: RB5

Reactive Black 5 is chosen as model compound for this study and it is one of the oldest reactive dyes. It is consumed very heavily in textile industries **(Arslan et al., 1999)** for the dying of cotton, woollen and nylon fabrics worldwide. It is reported to be toxic and cause allergic reactions of respiratory tract **(Fatemeh et al., 1990; Lars et al., 1997).**

To lower the cost of dye wastewater treatments, research was performed using cheap catalysts (foundry sand and fly ash) for photo-Fenton processes.

The aim of this work was to analyse the scope of using Foundry Sand and Fly Ash as iron source in the process of photo-Fenton for treating dye RB5.

1.5 Objectives of the study

Objectives undertaken in this study were-

- To determine the oxidative degradation and decolourization of RB5 in aqueous solution using FS and Fly ash as an iron source in photo-Fenton process
- To observe the influence of different reaction parameters like pH, H_2O_2 concentration, initial dye concentration, iron (FS, Fly ash and FS+ Fly ash) concentration on the photo-Fenton process.
- photo-Fenton study in slurry form using combination of FS and Fly ash as an iron source for the treatment,

To best of our knowledge, this is the first attempted study towards the use of FS and its mixture with Fly ash as alternative sources of iron in the photo-Fenton process for the treatment of RB5. The study enlightens the scope of using waste i.e. FS and Fly ash for the treatment of waste.

Chapter 2

Review of Literature

2.1 Contaminated water

The wastewater generated by the textile industry is rated as the most polluting among all industrial sectors considering both volumes discharged and effluent composition **(Vandevivere et al., 1998).** The presence of low concentrations of dyes in the discharge is highly visible and undesirable **(Nigam et al., 2000).** The dyes do not bind completely to the fabric and cause serious environmental problems. The release of these wastewaters in natural environments is mutagenic to human **(Chung et al., 1992)** and very problematic to aquatic life **(Chung et al., 1993).** The transmission of light and photosynthesis will be affected by the presence of colour in water and result in reduced aquatic diversity **(Raquel et al., 2008)**. Textile industry is one of the highest water consuming sectors, between 25 and 250 m^3 per ton of product depending on the processes and is the largest consumer of colorants for various dyeing, printing and finishing processes **(Chacon et al., 2006).** Wastewater from fabric dyeing industry is a considerable source of environmental contamination. The effluent from the dyeing and finishing processes is characterized by strong colour, high pH, high temperature, high COD, and low biodegradability **(Liakou et al., 1997).**

2.2 Dyes as pollutants

There are many kinds of dyes available in the market. Based on the chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Anthraquinone, phthalocyanine, triarylmethane and azo dyes are quantitatively the most important groups. The azo dyes, characterized by having an azo group consisting of two nitrogen atoms (-N=N-), are the largest class of dyes used in textile industry **(Zee, 2002).** Inside the azo dyes we have wide types of dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes. Between these, the most used are the reactive azo dyes. Additionally, these dyes are the most problematic pollutants of textile wastewaters. This fact occurs because after the reactive dyeing process is finished, more than 15% of the textile dyes is lost in wastewater stream during dyeing operation **(Park et al., 2003).**

In recent years, reactive dyes have been most commonly used due to their advantages such as better dyeing processing conditions and bright colours. Moreover, the use of reactive dyes is rapidly growing due to the increased use of cellulosic fibres. Generally reactive dyes contain functional groups such as azo, anthraquinone, phthalocyanine, formazin, and oxazine as chromophore. Among the reactive dyes, approximately 66% is unmetallized azo dye**.** The reactive site of the dyes reacts with functional group on fibres under influence of heat and alkali. One of the major factors determining the release of a dye into environment is its degree of fixation on the fibres. Reactive dye is hydrolyzed to some extent during application processes; some of reactive dyestuff is inactivated by a competing hydrolysis reaction. Consequently, the release of reactive dyes into dye bath effluent is exacerbated by their relatively low fixation (50-90%) to cellulosic fibres, compared with other dyes such as acid, basic, disperse and direct dye **(Reife et al., 1996).** Reactive dyes in dyeing wastewater have been identified as recalcitrant compounds since they contain high alkalinity, high concentration of organic materials and strong colour in comparison with other dyes. Unless colouring materials are properly removed, dye wastewater significantly affects photosynthetic activity in aquatic life due to reduced light penetration **(Kouba et al., 1994).**

2.3 Toxicity of dyes

In addition to being toxic, dye effluents also contain chemicals that are carcinogenic, mutagenic or teratogenic to various organisms **(Mathur et al., 2007).** This is especially serious because many chemicals can cause damage to genetic material without being expressed immediately **(Vogel, 1982).** Azo and nitro compounds have been reported to be reduced in sediments of aquatic bodies giving rise to potentially carcinogenic amines **(Chen, 2006).** Many dyes are made from known carcinogens like benzidine and are also known to accumulate, thus posing a serious threat **(Baughman et al., 1988).** Many dyes are also known to get reduced to toxic substances inside living organisms **(Weber et al., 1987).** The carcinogenicity of azo dyes, which constitute a significant proportion of textile dyes, is well known **(Umbuzeiro et al., 2005).** Some azo dyes have been linked to bladder cancer in humans; to splenic sacromas, hepatocarcinomas and nuclear anomalies in experimental animals and to cause chromosomal aberration in mammalian cells **(Mendevedev et al., 1988; Percy et. al., 1989).**

2.4 Conventional treatment technologies

The traditional treatment techniques for textile wastewaters, such as coagulation/flocculation, membrane separation (ultra filtration, reverse osmosis) or elimination by activated carbon adsorption, only do a phase transfer of the pollutant. Biological treatment is not a complete solution to the problem due to biological resistance of some dyes **(Lucas et al., 2006)**.

Both biological and physicochemical methods have been used for the decolorization and degradation of the organic compounds in dye wastewater. Typical dye wastewater treatment methods are coagulation/flocculation, adsorption and oxidation in combination with biological treatments **(Sarasa et al., 1998).** Combined treatment methods such as adsorption processes by various adsorbents, advanced oxidation processes (using H_2O_2, ozone, UV, etc.) and biodegradation (aerobic and anaerobic) have been also proposed for the treatment of reactive dye wastewater **(Karcher et al., 2001).** Coagulation and flocculation processes have been widely used as pre-treatments to remove suspended particles and colouring materials prior to biological treatment **(Torres et al., 1997).**

2.4.1 Physical methods

Physical methods include adsorption on activated carbon, peat, wood, fly ash, coal, silica **(Nigam et al., 2000)** or processes like membrane filtration, ion-exchange, coagulation **(Golob et. al., 2005)** and reverse osmosis **(Bastaki, 2004).** Coagulation is traditionally done using Aluminum (Al) or Iron (Fe) salts. Inorganic polymer flocculants are also currently in use **(Tang, 1990).** The chemical coagulation has been successfully used for treatment of textile effluents **(Zhu et al., 2007).** Biosorption has been studied by several researchers. Various agricultural wastes like rice husk, sugarcane bagasse, pinewood, corncobs, chitosan etc. can adsorb and accumulate dyes **(Crini, 2006; Ferrero, 2007).** Physical methods suffer with problems like excess sludge production. They are effective only when effluent volume is small. The disposal of the solid adsorbent itself becomes a big problem. Adsorption has been observed to be an effective process for colour removal from dye wastewater. Use of activated carbon has been found to be effective, but it is too expensive. Many studies have been undertaken to investigate the use of low-cost adsorbents such as peat, bentonite, steel-plant slag, fly ash, china clay, maize cob, wood shavings, and silica for colour removal **(Crini, 2006; Gupta et al., 2009).** These low-cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents. Therefore, there is a need to find new, economical, easily available and highly effective adsorbents.

2.4.2 Chemical methods

These involve oxidation using oxidising agents like Fenton’s reagent **(Slokar et al.,1997)**, ozone **(Gahr et al., 1994)**, sodium hypochlorite **(Lodha et al., 2007)** or photochemical methods and electrochemical degradation **(Awad et al., 2005).** Ozonation has been extensively used for remediation **(Tanja et al., 2003).** It has been shown that ozone cleaves the conjugated double bonds of the chromophore resulting in decolourisation. Prolonged ozonation can however, remove the toxic products **(Kandhraoui et al., 2009).** Immobilized TiO_2 has also been used for dye removal **(Mehmoodi et al., 2009).** Photocatalytic oxidation on immobilized TiO_2 in presence of solar irradiation and combined with electro chlorination has been successful in decolorization and toxicity reduction **(Wang et. al., 2008).** These processes often results in formation of toxic products **(Wang et. al., 2002).**

2.4.3 Biological methods

These involve microorganisms like fungi **(Barr et al., 1994)** and bacteria **(Banat et al., 1997).** Microbial treatment is cost effective and is receiving wide attention **(Zee et al, 2005).** Biological treatment may involve aerobic and anaerobic degradation by microorganisms. Biological methods are sometimes not suitable because of the structure of the dye molecule which may be non biodegradable. Also biological activity in liquid state fermentation is incapable of removing dyes continuously from the effluent. This is because; decolorization and fermentation process requires some time period and therefore the effluent has to be stored in large tanks for the process.

2.5 Advanced Treatment Technologies

Advanced oxidation processes (AOPs), considered as non-waste generating technologies, represent a robust alternative wastewater treatment for dye effluent when common wastewater treatment technologies such as sedimentation, adsorption, flocculation, filtration, reverse osmosis are insufficiently effective **(Huitle et al., 2009).** AOPs have been postulated as pretreatment step prior to biological treatment apart from disinfection and deactivation of pathogenic microorganism that are difficult to degrade biologically **(Anastasiou et al., 2009; Karimi et al., 2009; Erden et al., 2010; Mandal et al., 2010).** AOPs have the ability of exploiting the high reactivity of •OH radicals in driving oxidation processes **(Liotta et al., 2009).** The •OH radicals can be generated in situ through either one or the combination of chemical oxidation by using ozone, hydrogen peroxide with or without the radiation assisted sources such as ultrasounds, ultraviolet, solar visible and thermal. In more advance process, the •OH radicals can be generated by gamma radiation, microwaves, pulsed electron beam and the ferrate reagent **(Quan et al., 2007; Samanta, 2008; Wojnarovits et al., 2008; Huang et al., 2009; Mok et al., 2009; Rauf et al., 2009).** By tailoring the conditions of the reaction, •OH radicals which possess powerful oxidizing potential up to +2.8 V can attack a wide variety of toxic contaminants **(Devi et al., 2009).**

Advanced Oxidation Processes (AOPs), like Fenton and photo-Fenton processes, could be a good option to treat and eliminate textile dyes. These processes appear to have the capacity to completely decolorize and partially mineralize the textile industry dyes in short reaction time, as it was related by some studies **(Kang et al., 2002; Feng et al., 2003; Meric et al., 2004).** Advanced Oxidation Processes as shown in figure 2 are oxidation processes that offer a highly reactive, non-specific oxidant namely hydroxyl radicals, capable of destroying wide range of organic pollutants in water and wastewater **(Legrini et al., 1993).** Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton's reagent is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment **(Arnold et al., 1995).** In an acidic environment if hydrogen peroxide is added to an aqueous system containing an organic substrate and ferrous ions, a complex redox reaction will occur **(Lipczynska, 1991; Kuo, 1992; Walling, 1998).**

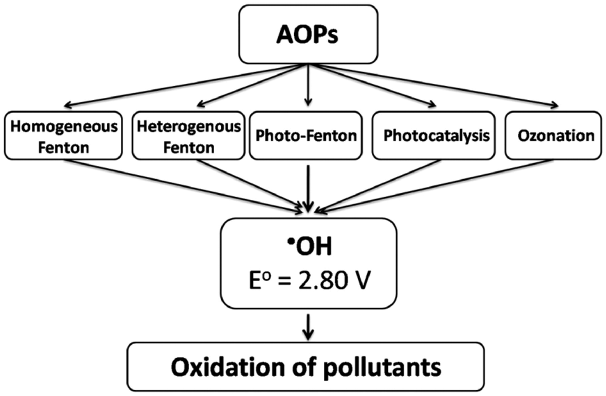


Figure2. Different Advanced Oxidation Processes

2.5.1 Photo-Fenton reaction

Photo-Fenton (UV light or visible light + Fenton) is a novel method in which water molecules undergo molecular fragmentation and release OH radical to oxidize the organic compounds **(Liang et al., 2007; Torres et al., 2007).** Generally, the most important advantage of photo-Fenton process is easier handling technologies without complex experimental apparatus. The most important reason that the photo-Fenton process can be effectively used in wastewater treatment is the synergistic effect by the coupled Fenton's reagent and light (solar light or UV illumination). Eq.1 shows the well-known Fenton reaction in solution. In this equation, Fe^{2+} is rapidly transferred to Fe^{3+} and produce OH radical. Recent reports indicate that the acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aqua complex, $Fe(H_2O)_5(OH)^{2+}$ (represented hereafter by $Fe(OH)^{2+}$), to providing a new importance source of OH radical. Further, the photolysis of $Fe(OH)^{2+}$ regenerates Fe^{2+} (Eqs.2 and 3), which means that the photo-Fenton reaction would need low Fe^{2+} concentration compared with the Fenton process **(Katsumata et al., 2008).** This UV illumination isolated Fe^{2+} can react subsequently with H_2O_2 and produce OH radical again (Eq. 1), and then a cyclic mechanism is established **(Torrades** et al., 2007; **Zhang et al., 2009)**. In addition, H_2O_2 can be isolated to two OH radicals by UV irradiation **(De et al., 1999);** therefore, a photo-Fenton process has been proven as a profitable method for destroying and oxidizing the refractory compounds.

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

$$Fe^{2+} + H_2O_2 \rightarrow Fe\,(OH)^{2+} + OH^{\cdot} \quad (2)$$

$$Fe\,(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\cdot} \quad (3)$$

The effluents from textile industry contain a variety of harmful chemicals. These chemicals severely affect the quality of water and environment. Quantitative measurement of these pollutants is not possible because they undergo chemical transformations in environment.

Various techniques have been suggested in literature for remediation of dyes containing waste water. Some of these are too expensive hence not viable. Those that are comparatively inexpensive are not very effective. Based on already reported studies, advanced oxidation process may be a viable option in this area as it gives considerable results and also supports use of low cost iron sources resulting in a low cost operation for treatment. Usage of different materials in photo-Fenton process as iron source was previously reported in literature and each of them have their own limitations. Here, we have attempted the use of two industry waste material (foundry sand and fly ash) as iron source in solar photo-Fenton process for the degradation of RB5 individually and in combination. This investigation may come out as inexpensive, easy to handle and viable alternative option for the treatment of RB5 polluted waste water.

2.6 Photo-Fenton reaction using alternative sources of iron

The use of a natural containing Fe-clay for the heterogeneous Fenton- like and photo-Fenton-like oxidation of two organic pollutants was carried out. A total phenol and tyrosol conversion was also obtained in less than 20 min by photo-Fenton-like oxidation. Characterization of the clay has shown that the major iron species present and responsible for the catalytic performance was Fe_2O_3. 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).**

(Li 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.

(**Song 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.

Iron-containing SBA-15 catalyst consisting of crystalline hematite particle oxides supported onto a mesostructured silica matrix has been shown as a promising catalyst for the treatment of phenolic solutions through photo-Fenton processes. The outstanding physicochemical properties make this material more attractive than unsupported commercial hematite iron oxide catalyst, leading to a better overall photocatalytic performance **(Martinez et al., 2005).**

(**Liu 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.

The system that was developed, based on Fenton oxidation with zero-valent iron and hydrogen peroxide for the degradation of six different classes of pesticides and chemical groups, proved to be efficient. The advantages of this system are rapid degradation, high degradation rates, simple handling, and low cost. In addition, it is an environmentally friendly and sustainable method because the source of the metal iron was swarf, a residue of a metallurgical activity. Besides, the aqueous complexes of ferric ions generated by this oxidation process during the treatment can start a new Fenton's reaction **(Guimaraes et al., 2013).**

(**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.

The iron (III) immobilized on Rice Husk Ash (RHA) has been tested and used as catalyst in decolorization of AR1 in Fenton-like process. The study showed that the heterogeneous Fenton-like process of Fe- RHA can decolorize AR1 effectively. The initial dye concentration, the increase in catalyst loading, and hydrogen peroxide concentration favor the decolorization efficiency **(Daud et al., 2010).**

Chapter 3

MATERIALS AND METHODS

In this chapter, materials and methods used in this study are described in details, including chemicals, instruments, shallow pond batch slurry reactor, analytical analysis and experimental procedures used.

3.1 Chemicals

In this study, azo dye RB5 (55% purity, Sigma- Aldrich) was used as model compound for treatment and structure of RB5 is shown below in figure 3. Distilled water was used throughout the investigations. Dye solution was prepared by dissolving requisite amount of dye in distilled water. H_2O_2 (30% w/v, Ranbaxy laboratories) was used as received without further purification. Foundry sand and Fly ash was received as a gift sample from local industry and used as such as received without any further modifications. For adjusting the pH, H_2SO_4 and NaOH were used and initial pH monitored by basic pH meter (Century instrument).

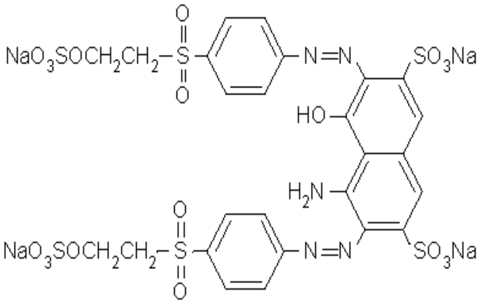


Figure 3. Structure of Reactive Black 5

3.2 Instruments Used

3.2.1 pH meter

pH of the solution was monitored by pH meter from the Century Instrument Company and adjusted with the help of 0.1 N NaOH and 0.1 N H_2SO_4. Instrument was calibrated by freshly prepared buffer solution (pH 4 to 9) time to time throughout the study.

3.2.2 Spectrophotometer

The spectrum was taken with UV-visible Spectrophotometer by Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer at 310 nm and 595 nm.

3.2.3 Magnetic stirrer

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

3.2.4 Air sparger

Air is continuously supplied during experiments in order to oxidize the organic matter.

3.2.5 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 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 RB5 solution (100 mgL^{-1}) was taken in this reactor at pH 3 and known amount of Fenton reagent (FS+H_2O_2) , (Fly Ash+H_2O_2) and (FS+Fly Ash+H_2O_2) were added. Samples were taken after regular intervals and analyzed for decolorization and degradation studies.

Figure 4. Shallow pond Slurry Batch reactor

3.4 Analytical analysis

The decolourization and degradation studies were performed with UV- visible Spectrophotometer (Hitachi V- 500 UV/VIS (Japan) double- beam spectrophotometer with RB5at 310 nm and 595 nm.

Scanning electron microscope (SEM) was used for the characterization of FS which we used in this study as alternative iron source. The result indicated absence of any heavy metal in FS and thus eliminates the risk of their leaching. A considerable amount of iron (23.16%) was reported which is utilized in photo-Fenton process. The reduction in the composition of iron and aluminium confirmed their participation in photo-Fenton reactions

For the characterization of Fly ash Scanning electron microscope (SEM) was used. The result indicated absence of any heavy metal in FS and thus eliminates the risk of their leaching. Although amount of iron detected was very less but there is presence of considerable amount of aluminium which can be used in the place of iron.

3.5 Experimental Procedure

3.5.1 Solar photo-Fenton using FS as iron source-

Reactive Black 5 solution of 100mgL^{-1} was prepared by distilled water. pH of the solution was adjusted to 3 using 0.1 N NaOH and 0.1 N H_2SO_4. 200 ml of sample was taken in immersion well reactor, 0.5 g of FS and 2.205 mM of H_2O_2 were added, air was also supplied by the aerator during experiment. Sample was taken in regular intervals of 15 min and filtered from 0.45 micron syringe filter. The concentration of these samples was detected by Spectrophotometer.

3.5.2 Solar photo-Fenton using Fly Ash as iron source-

Reactive Black 5 solution of 100mgL^{-1} was prepared by distilled water. pH of the solution was adjusted to 3 using 0.1 N NaOH and 0.1 N H_2SO_4. 200 ml of sample was taken in immersion well reactor, 0.1 g of Fly Ash and 2.205 mM of H_2O_2 were added, air was also supplied by the aerator during experiment. Sample was taken in regular intervals of 15 min and filtered from 0.45 micron syringe filter. The concentration of these samples was detected by Spectrophotometer.

3.5.3 Solar photo-Fenton using mixture of FS and Fly Ash as iron source-

Reactive Black 5 solution of 100 mgL^{-1} was prepared by distilled water. pH of the solution was adjusted to 3 using 0.1 N NaOH and 0.1 N H_2SO_4. 200 ml of sample was taken in immersion well reactor, 0.05 g of Fly Ash + 0.1 g of FS and 2.205 mM of H_2O_2 were added, air was also supplied by the aerator during experiment. Sample was taken in regular intervals of 15 min and filtered from 0.45 micron syringe filter. The concentration of these samples was detected by Spectrophotometer.

Chapter 4

RESULTS AND DISCUSSION

This chapter deals with results and subsequent discussions for the degradation of RB5 using Foundry Sand (FS), Fly ash and their combinations. Degradation as well as decolorization of RB5 was studied using FS and fly ash as iron source in photo-Fenton treatment. The purpose of studying decolorization during photo-Fenton treatment was to see the disappearance of colour imparting compounds from the waste water. However, it may contain toxic by products or there might be formation of toxic by products during treatment thus, there is a need to observe degradation of toxic compounds.

4.1 Absorption Spectra of RB5

The absorption spectrum of Reactive Black 5 was recorded with a "UV- vis. Spectrometer (Hitachi V- 500 UV/VIS Japan double-beam spectrometer). The samples were placed in a quartz cell and the spectra were recorded in the wavelength range of 250–700 nm. Total 2 peaks were observed in absorption spectra one is at 310 nm and another is at 595 nm as shown in Figure 5. Compound shows maximum absorbance at 595 nm (visible range) due to presence of colour and also at 310 nm (UV range) due to the presence of complex structure. Therefore reduction of RB5 concentration is measured at both wavelength 310 nm and 595 nm.

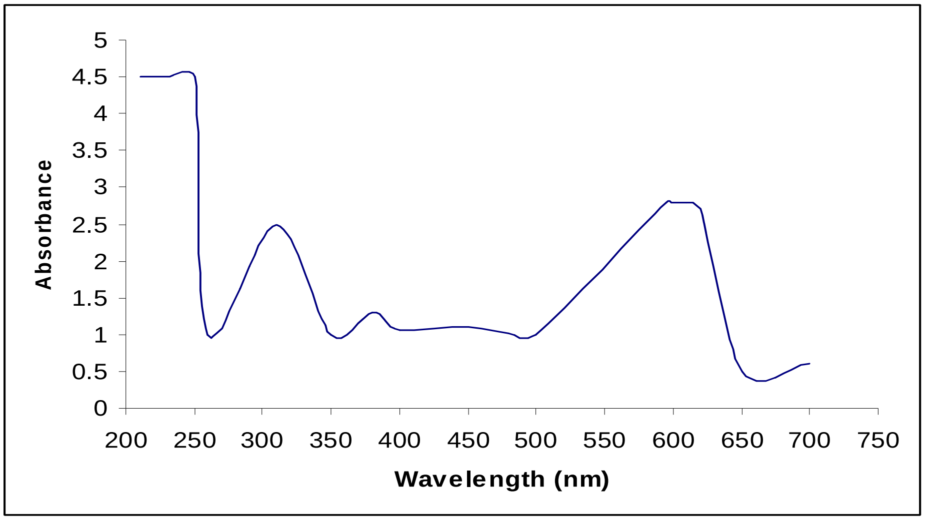


Figure 5. UV-Vis absorption spectrum of Reactive Black 5

4.2 Standard curve of RB5

Figure 6(a) and Figure 6(b) shows the standard curve for Reactive Black 5 which is prepared by plotting the absorbance of sample solution of varying known concentration ranging from 10ppm to 100 ppm at 310 nm and 595 nm against concentration. From this graph we can calculate unknown concentration for RB5 solution using formula i.e. y= mx where, y is absorbance, m is slope and x is concentration. Value of R^2 is 0.9985 and slope is 0.016 at wavelength 310 nm and R^2 is 0.9981 and slope is 0.0223 at wavelength 595 nm.

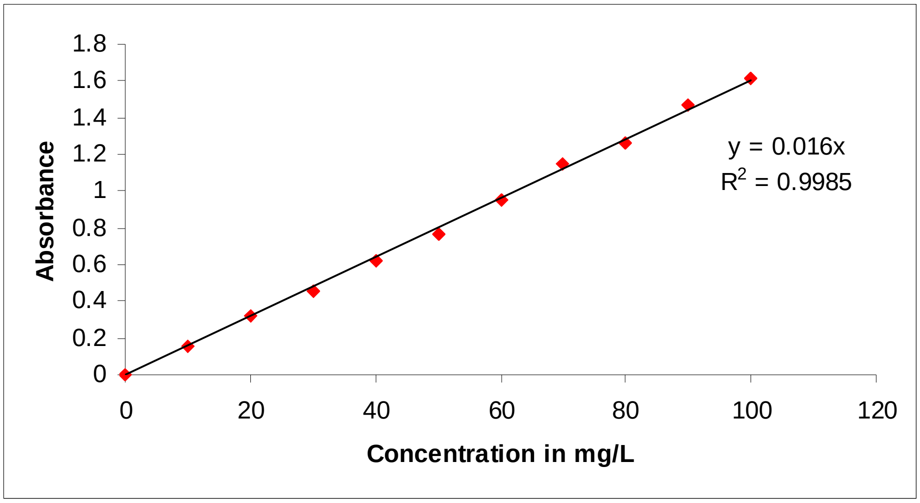


Figure 6(a). Standard curve of RB5 at wavelength 310 nm

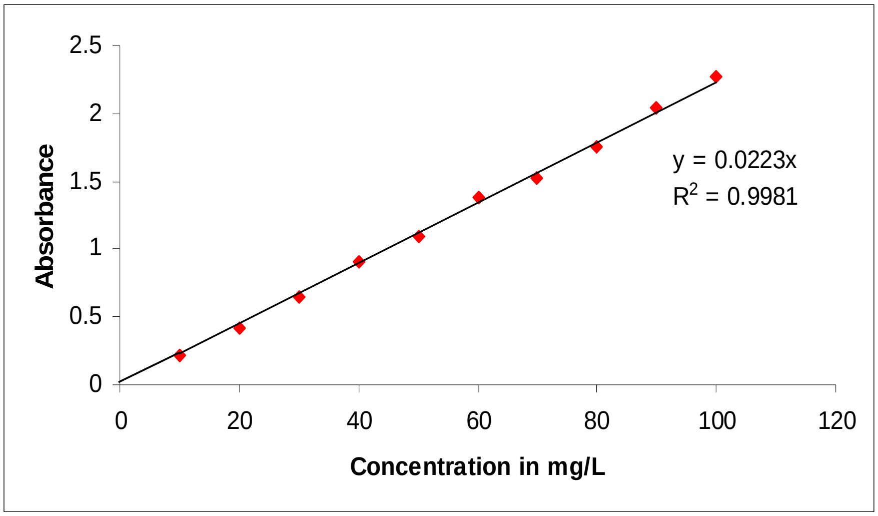


Figure 6(b). Standard curve of RB5 at wavelength 595 nm

4.3 Characterization of Foundry sand (FS)

Scanning electron microscope (SEM) was used for the characterization of FS which we used in this study as alternative iron source. The morphological image obtained by SEM was shown in figure 7(a). In order to determine the chemical composition, Energy-dispersive X-ray spectroscopy (EDS) was performed using same instrument and results was shown in Figure 7(b) and Table 1. The result indicated absence of any heavy metal in FS and thus eliminates the risk of their leaching. A considerable amount of iron (23.16%) was reported which is utilized in photo-Fenton process.

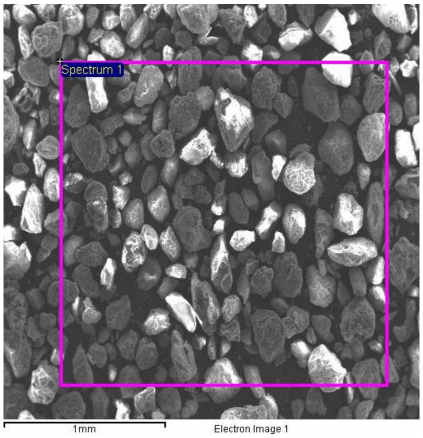


Figure 7(a) SEM micrograph of FS

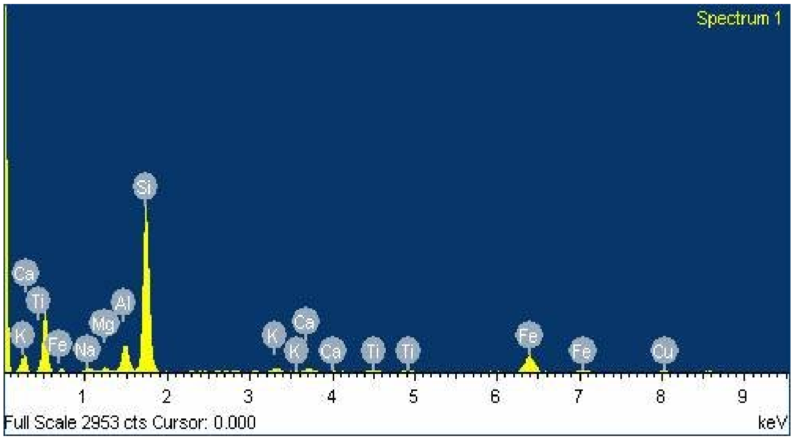


Figure 7(b) EDS pattern of FS

Table 1 Composition of Foundry Sand

Element	Weight%	Atomic%
Na K	1.93	2.73
Mg K	1.21	1.62
Al K	7.85	9.48
Si K	58.10	67.43
K K	1.77	1.48
Ca K	1.49	1.21
Ti K	1.36	0.93
Fe K	23.16	13.52
Cu K	3.13	1.60
Totals	100.00	

4.4 Photo Fenton studies using foundry sand as an iron source

4.4.1 Preliminary Experiments

Before the detailed studies, some preliminary experiments were performed to assess the catalytic activity of FS as a catalyst in the degradation of RB5 by heterogeneous photo-Fenton process. Preliminary experiments were carried out as follows: (1) presence of H_2O_2 only, (2) presence of FS only, (3) presence of sunlight only, (4) presence of FS along with H_2O_2, (5) presence of H_2O_2 and sunlight, (6) presence of FS and sunlight, and (7) presence of FS, H_2O_2 and sunlight. Degradation of 100 mgL^{-1} of RB5 with time is shown in figure 8(a) and figure 8(b). Low and negligible degradation and decolorization (less than 20%) in 120 min was achieved in the presence of H_2O_2 only, FS only and Sunlight only. This could be ascribed to limited production of OH radicals due to the insufficient availability of the resources in all three above cases required for the photo-Fenton process. From the results it is possible to observe that RB5 is resistant to the oxidation in the presence of FS + H_2O_2 and FS + Sunlight. In Fenton process (H_2O_2+ FS), 35% degradation in 90 min and 50% decolorization rates in 60 min were achieved. It is worth noting that 75% degradation in 90 min and decolorization efficiency of 85% in 60 min was achieved in the presence of FS as a heterogeneous catalyst, H_2O_2 and sunlight. This photo-Fenton result indicates that catalyst react with H_2O_2 in the presence of photons to generate OH radicals for the degradation of RB5. In the present work generation of OH radicals for degradation of RB5 was proposed via photo-Fenton mechanism using FS as an iron source.

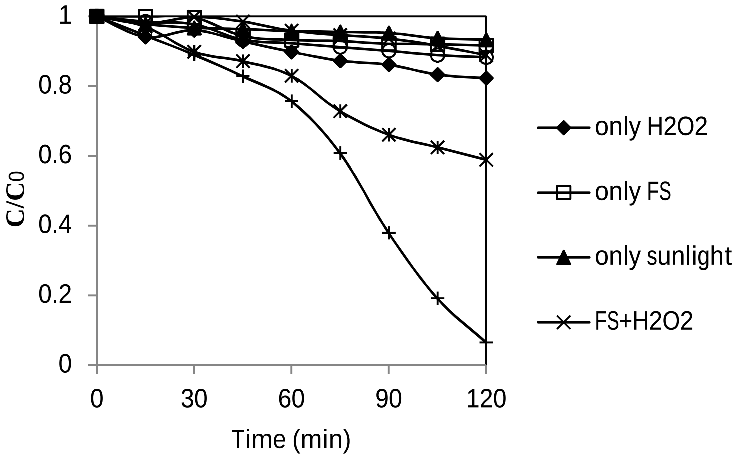


Figure 8(a). Preliminary experiments performed under different conditions to evaluate their efficiency towards degradation of RB5.

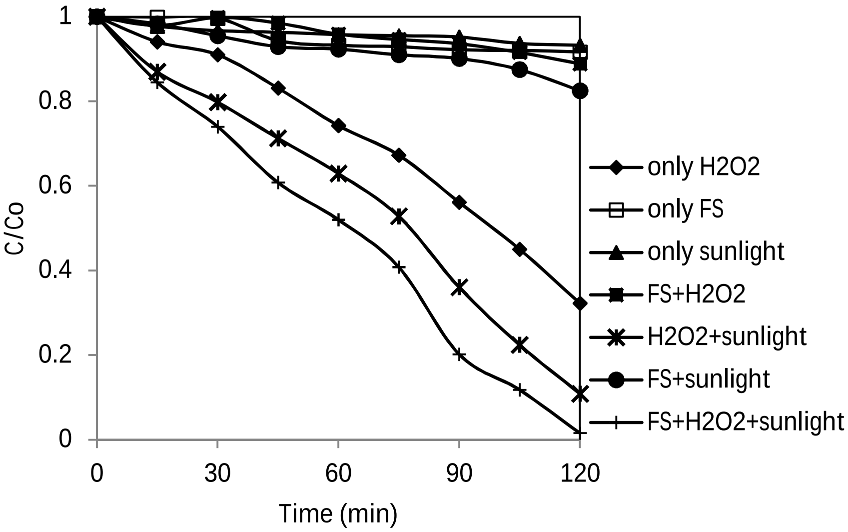


Figure 8(b). Preliminary experiments performed under different conditions to evaluate their efficiency towards decolorization of RB5.

4.4.2 Effect of variation of FS

FS was used as an iron source in varying concentrations ranging from 0.1 gm to 1.0 gm during the photo-Fenton treatment process while maintaining the other parameters constant. The amount of FS is one of the main parameters that influence the photo-Fenton process. The results shown in Figure 9(a) and 9(b) indicate that initial increase of FS till 0.5 gm increases degradation and decolorization of the dye. The lower degradation capacity of FS at small concentration is probably due to the lowest HO radical production available for oxidation. Further increase of FS dosage from 0.5 gm to 1.0 gm, degradation and decolorization of dye decreases. This reduction can be explained by OH radicals scavenging either by the reaction with hydrogen peroxide or by the reaction with Fe^{+2} as expressed in the equations **(Madhavan J. et al., 2010)**:

$$H_2O_2 + OH^{\bullet} \quad \rightarrow \quad H_2O + OH_2^{\bullet}$$

$$Fe^{+2} + OH^{\bullet} \quad \rightarrow \quad OH^{\bullet} + Fe^{+3}$$

The effective degradation (90%) within 90 min and decolorization (90%) within 60 min was achieved at 0.5 gm FS dosage.

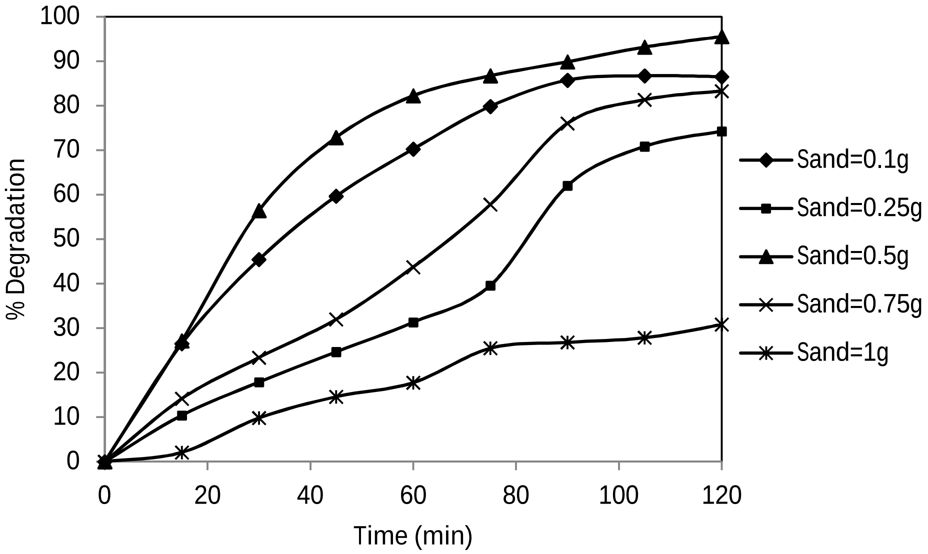


Figure 9(a). Percentage degradation of RB5 at varying concentration of FS at wavelength 310 nm.

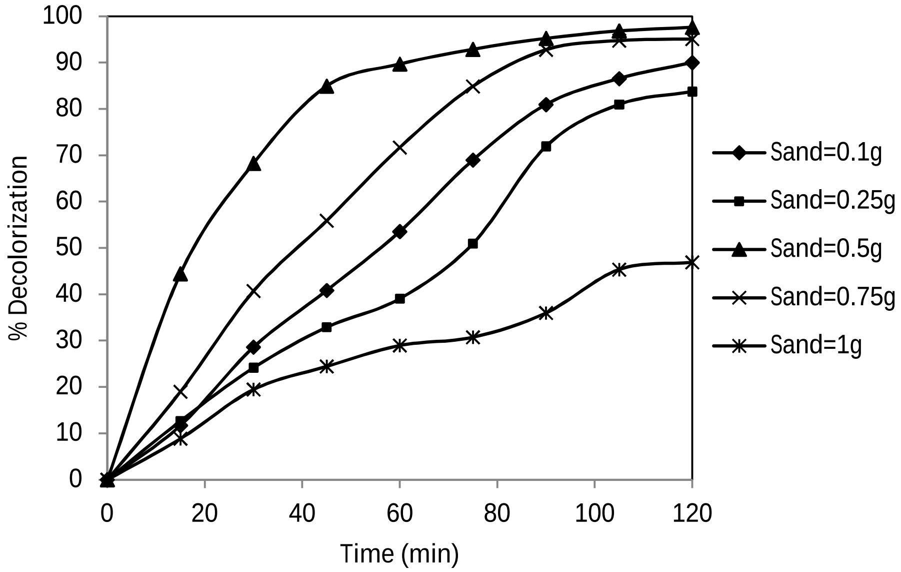


Figure 9(b). Percentage colour removal of RB5 at varying concentration of FS at wavelength 595 nm.

4.4.3 Effect of H_2O_2 concentration

Figure 10(a) and 10(b) shows the degradation and decolorization of RB5 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 0.0 mM to 8.82 mM into the dye solution at fixed FS and pH. Dye removal increases with the increasing dosage of H_2O_2 till 2.2 mM after that percentage of removal becomes constant till 6.61 mM and then decreases with the increasing dosage of H_2O_2. This decrease is due to the fact of scavenging of $OH^\bullet$ by H_2O_2 **(Walling, 1975)**, can be expressed by the equation:

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

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

Effective degradation (90%) was achieved within 70 min while decolorization (90%) of dye solution was achieved within 45 min of reaction at optimum dose 2.2 mM of H_2O_2.

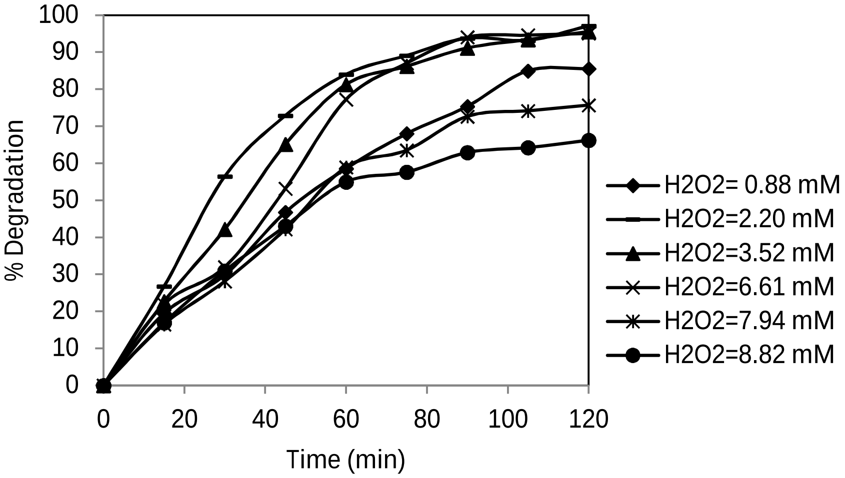


Figure 10(a). Percentage degradation of RB5 at varying concentration of H_2O_2 at wavelength 310 nm

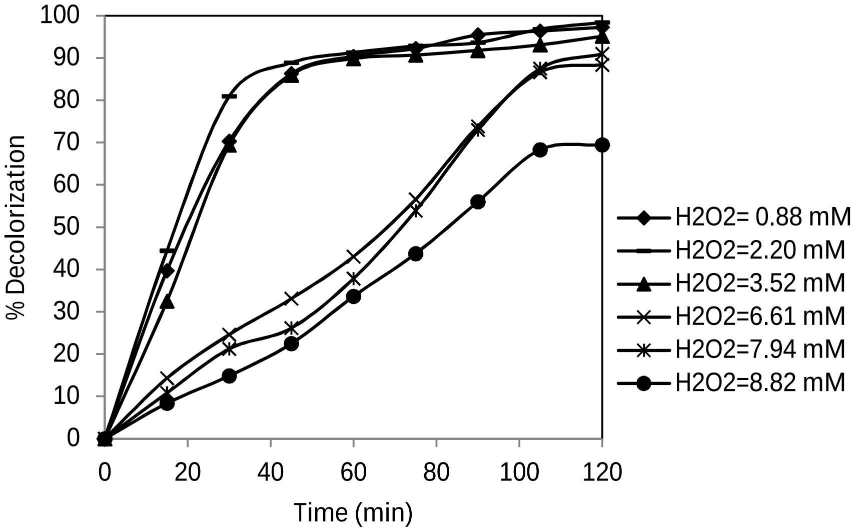


Figure 10(b). Percentage colour removal of RB5 at varying concentration of H_2O_2 at wavelength 595 nm

4.4.4 Effect of pH

The effect of pH on RB5 degradation and decolorization is shown in Figure 11(a) and 11(b). The figure shows that pH significantly influences the conversion of RB5. The pH of the reaction was varied in between pH 2 to 7. 90% degradation and decolorization efficiency was achieved at pH 3 for the reaction time of 70 min and 45 min respectively. At pH 2, nearly similar results were observed. Further increment in the pH from 3 leads to reduction in degradation (18%) and decolorization (28%) efficiencies. This behaviour could be explained by the formation of ferric hydroxo complexes during the reaction, which blocks the decomposition of hydrogen peroxide catalyzed by the ferrous iron **(Faust et al., 1990).**

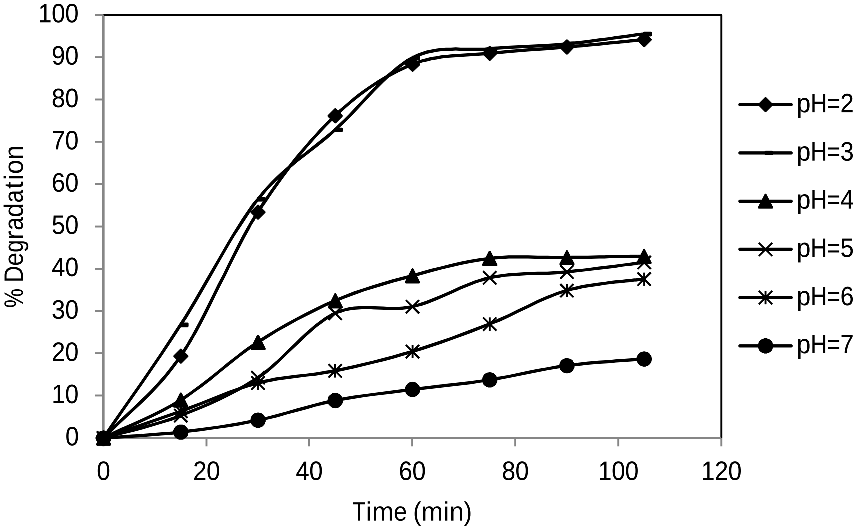


Figure 11(a). Percentage degradation of RB5 at varying of pH at wavelength 595 nm.

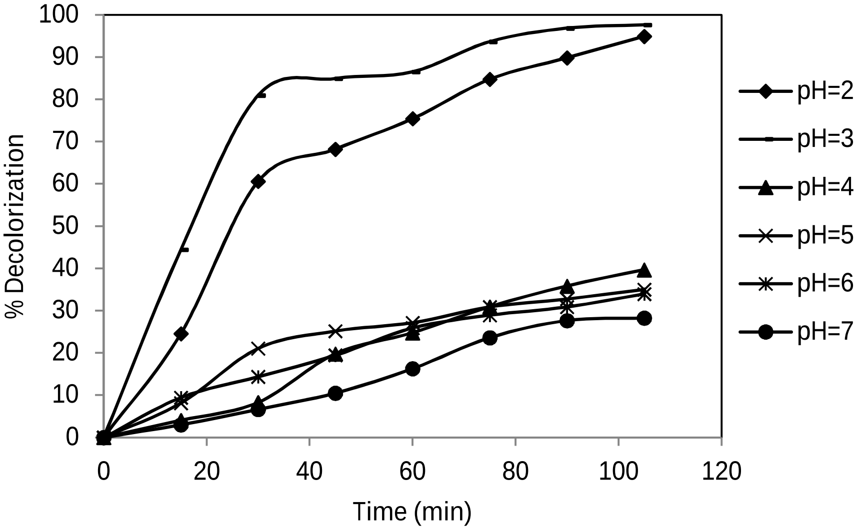


Figure 11(b). Percentage colour removal of RB5 at varying of pH at wavelength 595 nm.

4.4.5 Effect of dye concentration

The effect of initial dye concentration of aqueous solution of RB5 on the photo-Fenton processes was investigated, since pollutant concentration is an important parameter in wastewater treatment. The influence of the concentration is shown in Figure 12(a) and 12(b) from there it can be illustrated that the extent of decolorization and degradation with the increase in the initial dye concentration. Increase of dye concentration from 25mgL^{-1} to 100mgL^{-1}, increases the degradation efficiency from 75% to 90% in 70 min and decolorization efficiency from 60% to 90% within 45 min. It is due to the fact that; increase in dye concentration, increases the number of dye molecule which increases the probability of collision between dye molecule and oxidizing species, which lead to enhancement in the degradation efficiency **(Kitis et al., 2007)**. Further increment in dye concentration may leads to decrease in degradation and decolorization efficiency because increment in dye molecule concentration may obstructs the penetration of photons entering into the solution **(Feng et al., 2003)**.

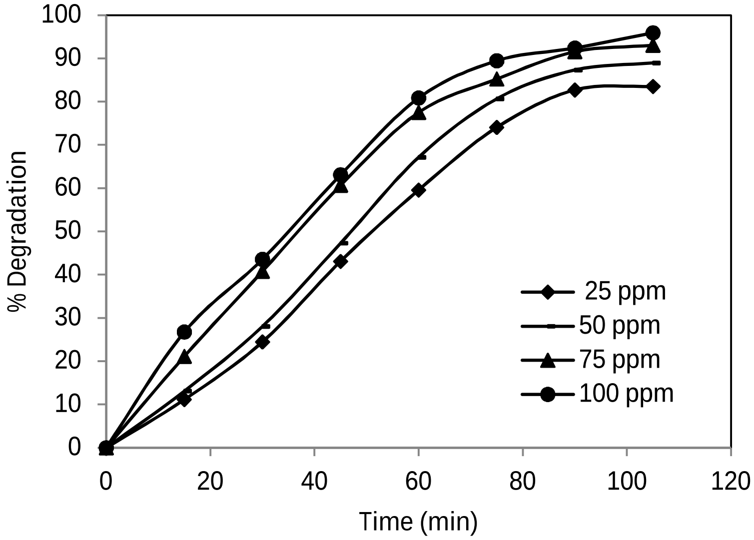


Figure 12(a). Percentage degradation of RB5 at wavelength 310 nm at varying concentration of RB5 and other parameters were fixed.

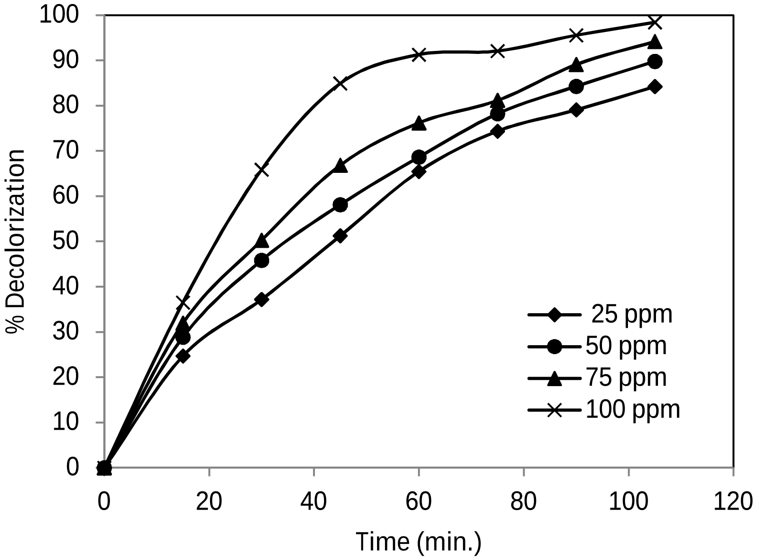


Figure 12(b). Percentage colour removal of RB5 at wavelength 595 nm at varying concentration of RB5 and other parameters were fixed.

4.4.6 Conclusion Remarks

The above study indicated the potential use of FS as an alternative source of iron in photo-Fenton process for the treatment of dye RB5. Effect of various reaction parameters on the degradation and decolorization efficiency was observed. The optimized parameters came out to be H_2O_2= 2.2 mM, FS dose= 0.5 g, pH 3, initial dye concentration= 100 mgL^{-1} where 90% degradation and decolorization efficiency was achieved in 75 min and 45 min respectively. The SEM- EDS used for FS is shown in Figure3. The reduction in the composition of iron and aluminium confirmed their participation in photo-Fenton reactions **(Tony et al., 2008)**. During photo-Fenton treatment with FS, these ions might have leached into the solution and subsequently used for degradation studies in the presence of H_2O_2.

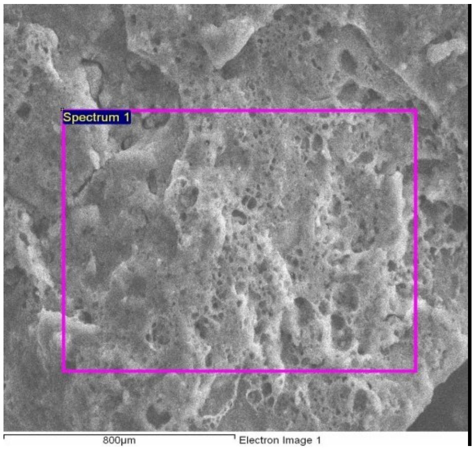


Figure 13(a) SEM micrograph

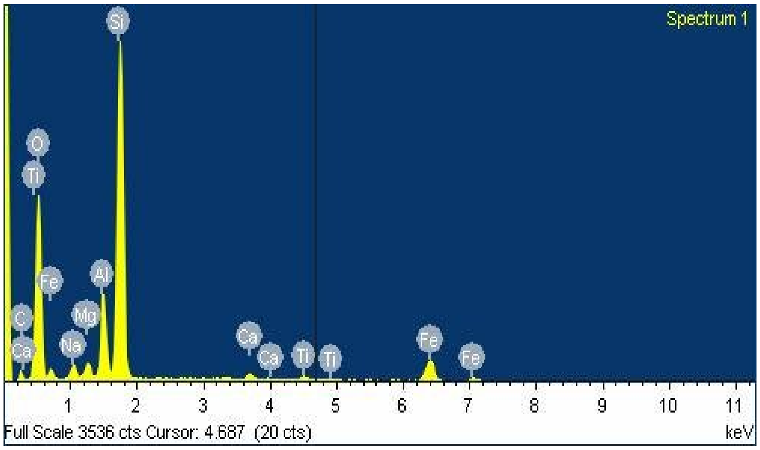


Figure 13(b) EDS pattern of FS after used in photo-Fenton process

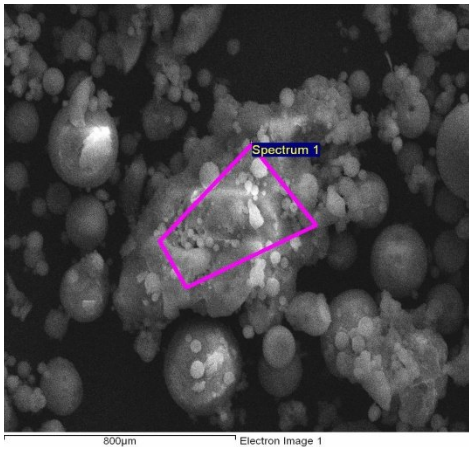
Table 2. Composition of FS after used in photo-Fenton process

Element	Weight%	Atomic%
C K	10.87	16.95
O K	50.50	59.12
Na K	1.42	1.16
Mg K	1.06	0.82
Al K	5.49	3.81
Si K	23.37	15.58
Ca K	0.64	0.30
Ti K	0.51	0.20
Fe K	6.15	2.06
Totals	100.00	

4.5 Photo-Fenton studies using fly ash as an iron source

4.5.1 Characterization of Fly Ash

For the characterization of Fly ash Scanning electron microscope (SEM) was used. The result obtained by SEM was shown in figure 14(a). In order to determine the chemical composition, Energy-dispersive X-ray spectroscopy (EDS) was performed using same instrument and results was shown in Figure 14(b) and Table 2. The result indicated absence of any heavy metal in FS and thus eliminates the risk of their leaching. Although amount of iron detected was very less but there is presence of considerable amount of aluminium which can be used in the place of iron as stated in literature **(Tony et al., 2008)**



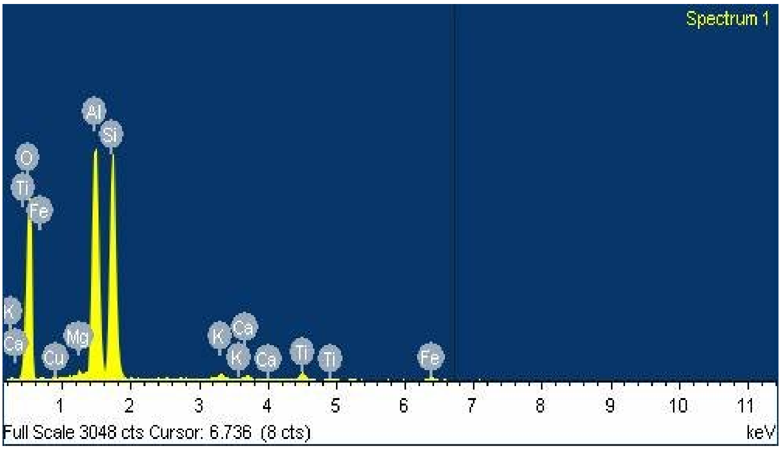


Figure 14(a) SEM micrograph

Figure 14(b) EDS pattern of Fly ash

Table 3 Composition of Fly ash

Element	Weight%	Atomic%
O K	55.87	69.45
Mg K	0.42	0.35
Al K	17.66	13.02
Si K	21.85	15.47
K K	0.67	0.34
Ca K	0.50	0.25
Ti K	1.33	0.55
Fe K	1.00	0.35
Cu K	0.70	0.22
Totals	100.00	

4.5.2 Preliminary Experiment

All the possible combinations of reaction component of photo-Fenton process were tested to compare their catalytic activity in degradation and decolorization of aqueous solution of RB5. The preliminary studies were performed under the conditions: (1) presence of H_2O_2 only, (2) presence of Fly Ash only, (3) presence of sunlight only, (4) presence of Fly Ash along with H_2O_2, (5) presence of H_2O_2 and sunlight, (6) presence of Fly Ash and sunlight, and (7) presence of Fly Ash, H_2O_2 and sunlight. As shown in figure 15(a) and 15(b)., the degradation of dye was less than 20% in the only presence of H_2O_2, around 15% in the presence of fly ash only, negligible when exposed to only sunlight, 22% in the presence of fly ash along with H_2O_2, 50% with sunlight and H_2O_2, very less in the presence of fly ash and sunlight, 87% in the presence of fly ash, H_2O_2 and sunlight within 120 min.. Less and negligible degradation rates in the presence of H_2O_2 only may be due to its limited oxidation capability as compared to OH radicals. The degradation achieved in the presence of fly ash only may be due to adsoption by fly ash. From the results it can be concluded that photo-Fenton process alone is more efficient than other individual experimental conditions. On this basis we choose photo-Fenton treatment for the degradation studies of RB5.

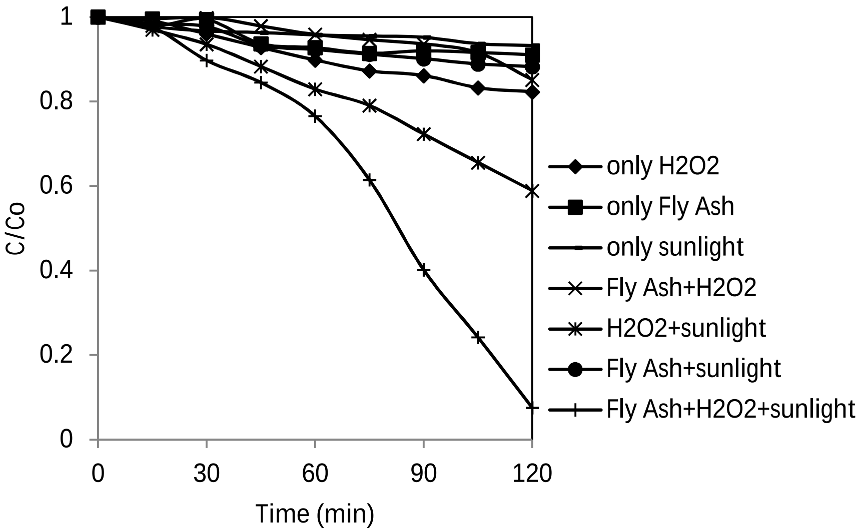


Figure 15(a). Preliminary experiments performed under different conditions to evaluate their efficiency towards degradation of RB5

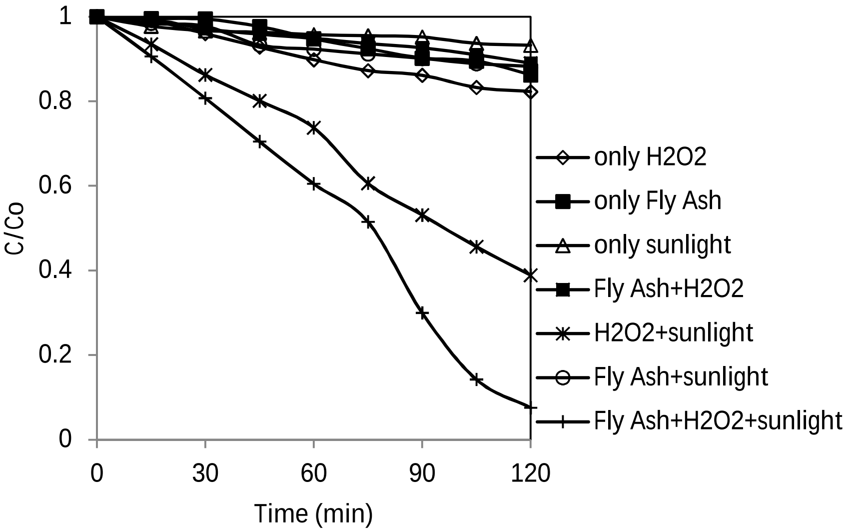


Figure 15(b). Preliminary experiments performed under different conditions to evaluate their efficiency towards decolorization of RB5.

4.5.3 Effect of variation of fly ash

On the degradation of the dye the effect of the fly ash concentration added was observed in the range of 0.05 gm to 1 gm and shown in figure 16(a) and 16(b). With the increase of fly ash dose, degradation and decolorization efficiency increases till a certain limit (0.1 gm) after that decreased efficiencies were observed. The optimum amount of fly ash was 0.1 gm resulting in 92% degradation in 75 min and 97% decolorization in 15 min. At higher fly ash concentrations, a relative decrease in degradation and decolorization rates were observed may be due to the adsorption of both H_2O_2 and dye molecule on separate particles rather than at the adjacent sides of the same particle and thereby not reacting to each other **(Chaudhuri et al., 2000).** This reduction can also be explained due to the fact that, at higher concentration of iron than the optimum, the hydroxyl radical initial formation rate was so high that most of them were consumed by the side reactions before they could be utilized for the mineralization of the compound **(Catalkaya et al., 2005**).

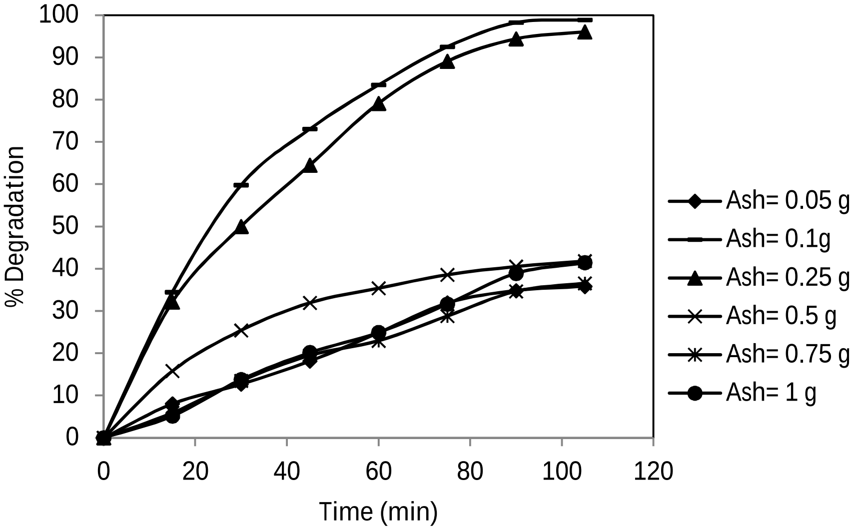


Figure 16(a). Percentage degradation of RB5 at varying concentration of Fly Ash at wavelength 310 nm.

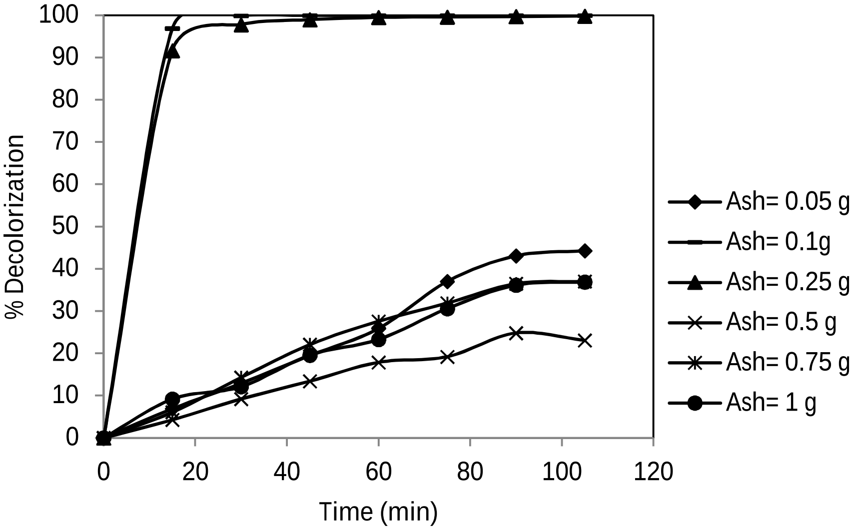


Figure 16(b). Percentage colour removal of RB5 at varying concentration of Fly Ash at wavelength 595 nm.

4.5.4. Effect of H_2O_2 concentration

In the presence of fly ash, the influence of H_2O_2 concentration on the heterogeneous photo-Fenton degradation of the dye was also investigated with different levels of H_2O_2 concentration (0.44, 0.88, 2.2, 6.61 and 8.82 mM) while keeping other operating parameters constant (Fly

Ash= 0.1 gm, pH 3, Initial concentration of dye= 100 ppm). From the figure 17(a) and 17(b) it can be illustrated that the effective degradation (90%) within 30 min and decolorization (95%) within 10 min of the dye occurred at the dose of 2.2 mM. Degradation rate of the dye increases as the H_2O_2 concentration increases until 2.2 mM which is the optimum H_2O_2 concentration after further increment in the dosage of H_2O_2, leads to decrease in degradation rates. This reduction may be explained by the so-called hydroxyl radical scavenging effect **(Hsueh et al., 2005).**

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet}\ OH_2^{\bullet}$$

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

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

Based on this study, 2.2 mM of H_2O_2 dose was selected for further experiments.

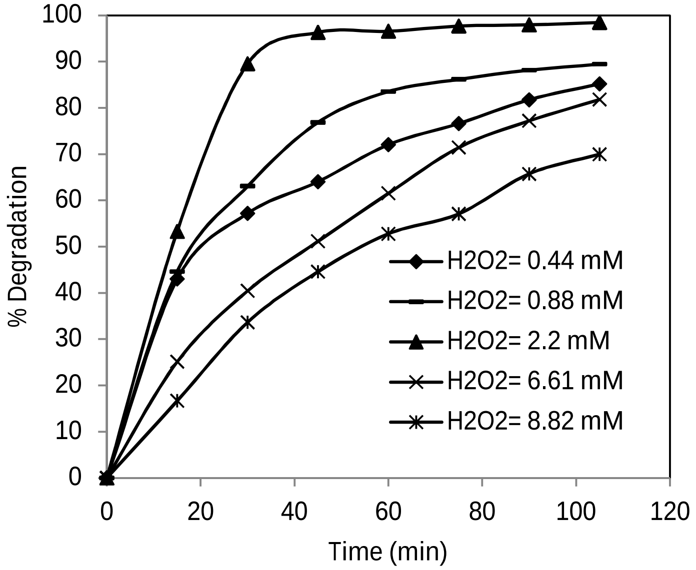


Figure 17(a). Percentage degradation of RB5 at varying concentration of H_2O_2 at wavelength 310 nm

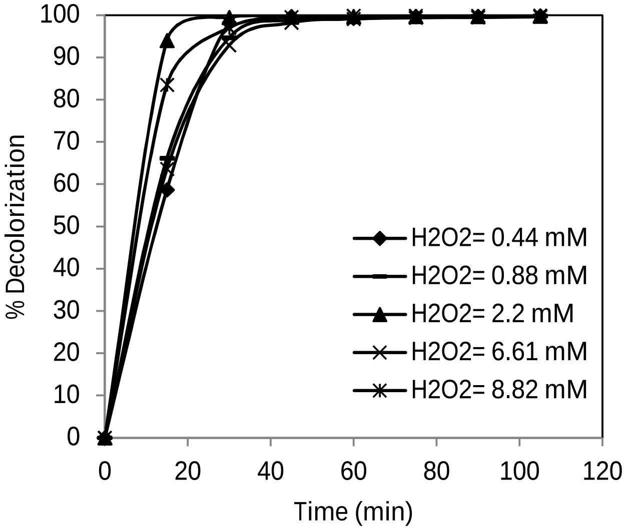


Figure 17(b). Percentage colour removal of RB5 at varying concentration of H_2O_2 at wavelength 595 nm.

4.5.5 Effect of pH

The effect of pH value of the solution on the degradation and decolorization of dye was studied in the range of pH 2 to pH 6 and the results were shown in the figure 18(a) and 18(b). The results indicate the influence of pH value on generation of hydroxyl radicals and thus the oxidation efficiencies. The optimum pH was found to be about 3 resulting in 90% degradation within 30 min and 93% decolorization rates within 15 min 99%. At pH values higher than 4, the removal rate of RB5 decreases because precipitation of iron as hydroxide leads to decrease in the transmission of the photons **(Faust B.C et al., 1990).**

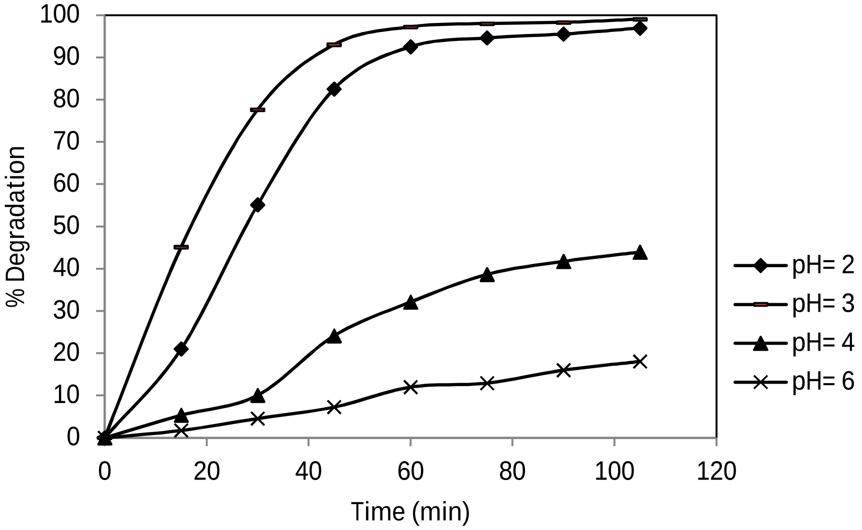


Figure 18(a). Percentage degradation of RB5 at varying of pH at wavelength 595 nm.

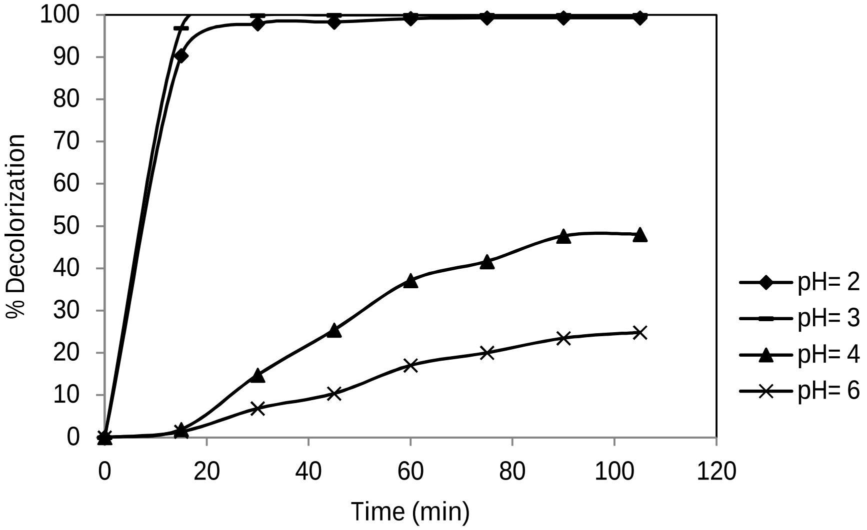


Figure 18(b). Percentage colour removal of RB5 at varying of pH at wavelength 595 nm.

4.5.6 Effect of dye concentration

The effect of initial dye concentration on photo-Fenton process was observed because it is very important from an application point of view. The initial dye concentration was varied in between 25 mgL^{-1} to 100 mgL^{-1} and its influence on degradation and decolorization shown in figure 19(a) and 19(b). From the results it can be concluded that with the increase in initial dye concentration degradation and decolorization efficiency decreases. The decrease in removal rate is due to the presumed reason that when the initial concentration of RB5 increases, the H_2O_2 concentration remains constant so the number hydroxyl radical remains constant for all the dye molecules hence the degradation efficiency diminishes **(Modirshala et al., 2007).**

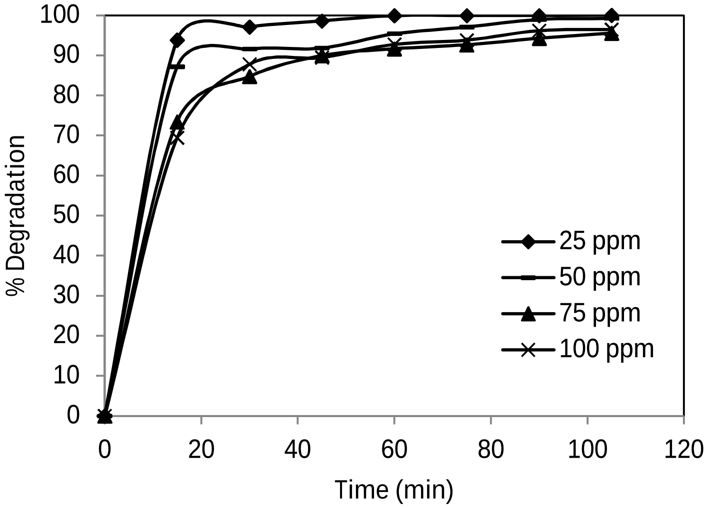


Figure 19(a). Percentage degradation of RB5 at wavelength 310 nm at varying concentration of RB5 and other parameters were fixed.

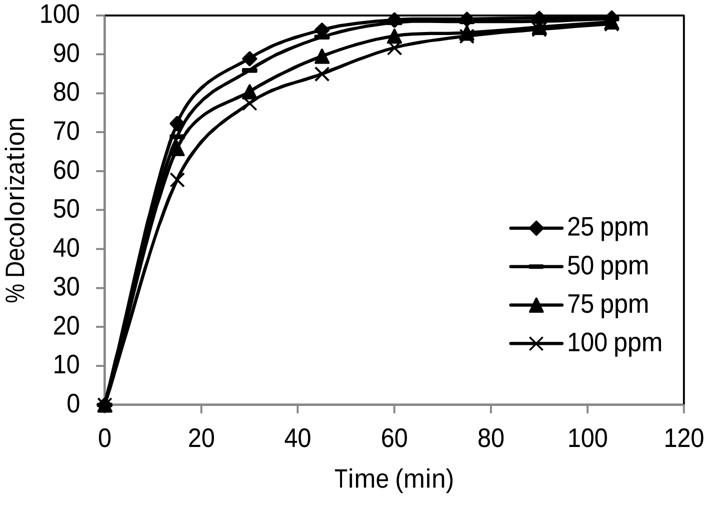


Figure 19(b). Percentage colour removal of RB5 at wavelength 595 nm at varying concentration of RB5 and other parameters were fixed.

4.5.7 Conclusion Remarks

The above study indicated the potential use of Fly ash as an alternative source of iron in photo-Fenton process for the treatment of dye RB5. Effect of various reaction parameters on the degradation and decolorization efficiency was observed. The optimized parameters came out to be H_2O_2= 2.2 mM, Fly ash dose= 0.1 g, pH 3, initial dye concentration= 100 mgL^{-1} where 90% degradation within 30 min and 93% decolorization rates within 15 min was achieved. The SEM-EDS used for Fly ash is shown in Figure20 (a), 20(b) and Table 3. The reduction in the composition of iron and aluminium confirmed their participation in photo-Fenton reactions **(Tony et al., 2008)**.

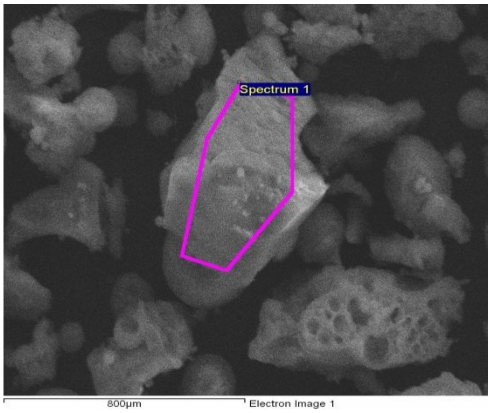


Figure 20(a) SEM micrograph

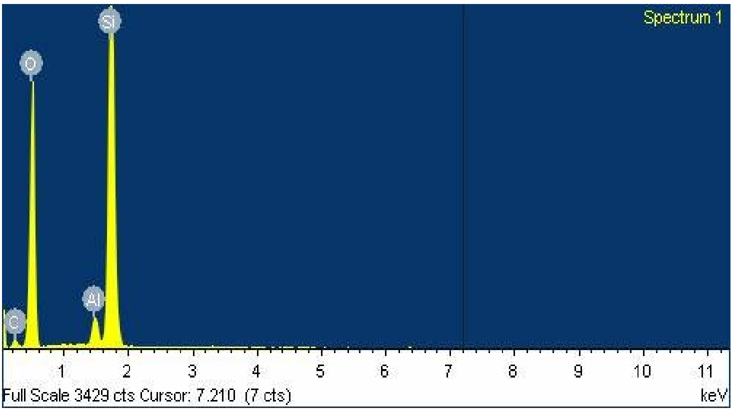


Figure 20(b) EDS pattern of Fly ash after used in photo-Fenton process

Table 4. Composition of FS after used in photo-Fenton process

Element	Weight%	Atomic%
C K	8.33	12.38
O K	61.12	68.17
Al K	1.54	1.02
Si K	29.02	18.44
Totals	100.00	

4.6 Photo-Fenton studies using mixture of foundry sand and fly ash as iron source

4.6.1 Effect of FS concentration keeping Fly ash constant

To ascertain the effect of FS in oxidizing RB5, a series of experiments were conducted by varying FS concentration in the ratio of Ash : Sand= 1:1, 1:2, 1:4, 1:6, 1:8, 1:10 and 1:12. The influence of FS dosage on degradation and decolorization efficiency is illustrated in figure 21(a) and 21(b). The degradation and decolorization rate of RB5 decreased with increasing amounts of FS. 99% degradation and decolorization rates were achieved in 120 min at the ratio Ash:Sand= 1:2 where amount of Ash and FS were 0.05 g and 0.1 g respectively.

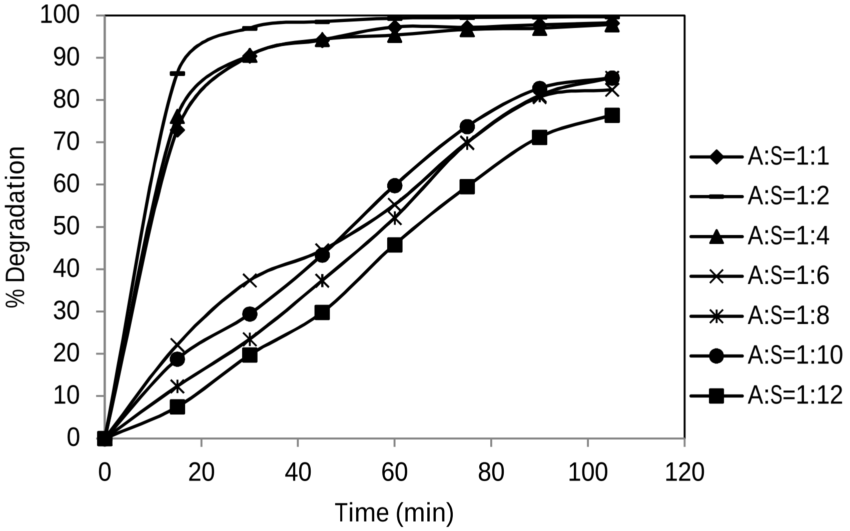


Figure 21(a). Percentage degradation of RB5 at wavelength 310 nm at varying concentration of FS and other parameters were fixed (A:S is Fly Ash: FS).

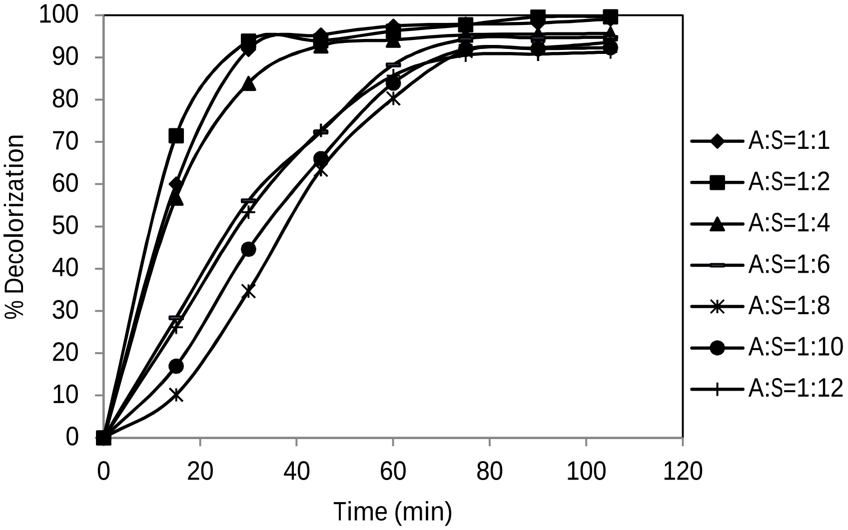


Figure 21(b). Percentage colour removal of RB5 at wavelength 595 nm at varying concentration of FS and other parameters were fixed (A:S is Fly Ash: FS).

4.6.2 Effect of Fly Ash concentration keeping FS constant

The effect of added ratio of fly ash keeping FS and other parameters constant in solution on the degradation and decolorization of RB5 was investigated in the ratio range of Sand : Ash= 1:1, 5:1, 5:2, 5:3, 5:4 and 10:1 and the results were presented in Figure 22(a) and 22(b). The results indicated that the extent of degradation and decolorization was significantly influenced by the dosage of fly ash. Decrease in the degradation and decolorization efficiency was observed with increasing amount of fly ash. The optimal ratio value for the degradation (92%) in 60 min and decolorization (90%) in 30 min for the dye was achieved at Sand : Ash= 10:1 where FS and Fly ash were taken 0.5 g and 0.05 g respectively.

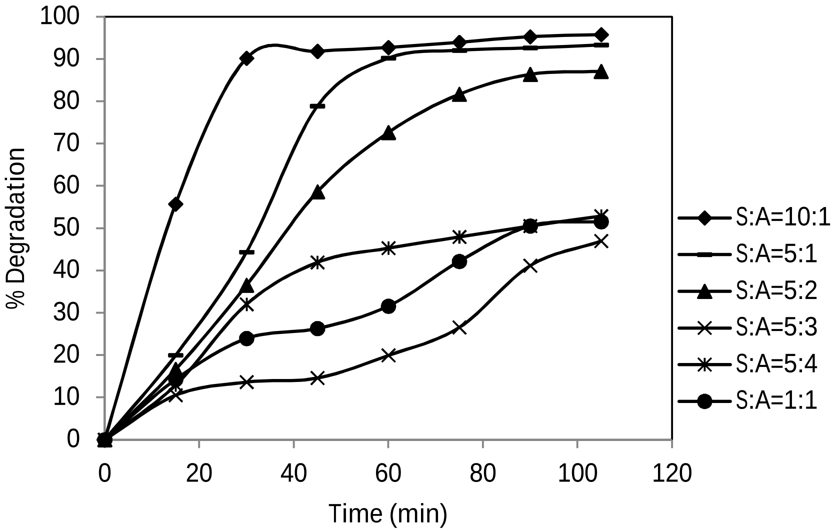


Figure 22(a). Percentage degradation of RB5 at wavelength 310 nm at varying concentration of Fly Ash and other parameters were fixed (S:A is FS: Fly ash)

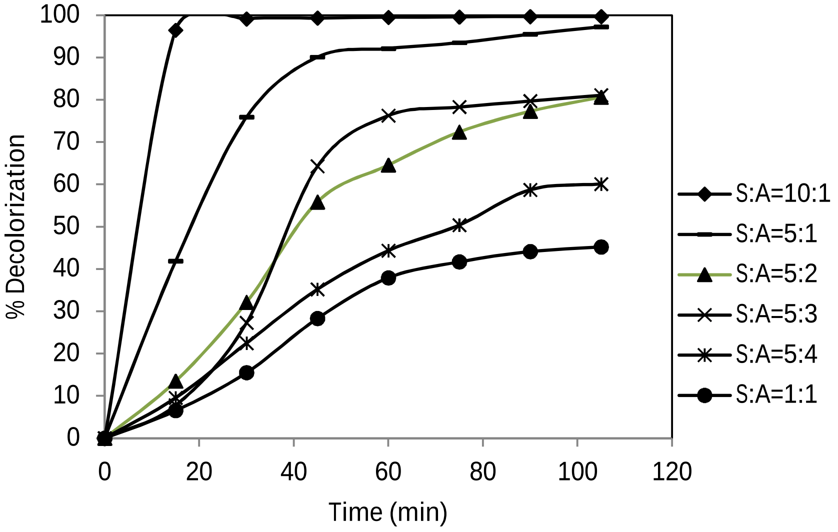


Figure 22(b). Percentage colour removal of RB5 at wavelength 595 nm at varying concentration of Fly Ash and other parameters were fixed (S:A is FS: Fly ash)

4.6.3 Conclusion Remarks

The above study indicated the potential use of combination of FS with Fly ash as an alternative source of iron in photo-Fenton process for the treatment of dye RB5. Effect of various reaction parameters on the degradation and decolorization efficiency was observed. This study concluded that combination of FS and fly ash gave better results in terms of degradation and decolorization along with the reduction in treatment time. For combination of FS and fly ash, degradation (90%) after 25 min and decolorization (97%) within 10 min was achieved whereas, for the same degradation (90%) and decolorization (90%) FS alone took 70 min and 45 min respectively and Fly ash took 30 min for 90% degradation and 15 min in 93% decolorization.

Thus, combination gave the better prospects for the use of waste materials like FS and fly ash to be used as potential iron source in photo-Fenton process as pre or post treatment options for the degradation of priority pollutants like dyes.

Chapter 5

Conclusion

To best of our knowledge this is the first attempted study for using FS and its combination with Fly ash as heterogeneous catalyst in solar photo-Fenton process on the compound RB5. The heterogeneous catalyst has successfully demonstrated its capabilities to undergo photo-Fenton process and degrade and decolorize RB5.

- While using FS as heterogeneous catalyst maximum degradation and decolorization 95% and 97% respectively was achieved when FS= 0.5 g, H_2O_2 concentration= 2.2 mM, pH 3, initial dye concentration= 100 mgL^{-1} in 120 min.
- While using Fly Ash as heterogeneous catalyst 99% degradation and decolorization rate was achieved when Fly Ash= 0.1 g, H_2O_2 concentration= 2.2 mM, pH 3, initial dye concentration= 100 mgL^{-1} in 120 min.
- When combination of FS and Fly Ash was tried 99% degradation and decolorization of RB5 was achieved in 120 min when Ash : Sand= 1:2, H_2O_2 concentration= 2.2 mM, pH 3, initial dye concentration= 100 mgL^{-1}.

It is a viable option to have a mixture of FS and fly ash as heterogeneous catalyst in photo-Fenton process as it leads to the reduction of amount of catalyst required for the Photo-Fenton reaction. Amount of FS and Fly ash gets reduced from 0.5 g to 0.1 g and 0.1 g to 0.05 g respectively when used in combined form. The study enlightens the scope of using waste i.e. FS and Fly ash for the treatment of waste.

With these positive results from the proposed study, efforts can be made in future for effective reactor design using FS and Fly ash and to implement this process in immobilized form for the treatment of bio recalcitrant compounds. With little modifications this technology can be used as pre and post treatment options in conjunction with conventional treatment.

REFERENCES

Anastasiou N., Monou M., Mantzavinos D., Kassinos D., (2009). Monitoring of the quality of winery influents/effluents and polishing of partially treated winery flows by homogeneous Fe(II) photo-oxidation, Desalination 248:836–842.

Arnold S.M., Hickey W.J., Harris R.F., (1995). Degradation of atrazine by Fenton's reagent: condition optimization and product quantification. Environmental Science and Technology 29:2083-9.

Arslan A., Balcioglu T., Tuhkanen, (1999). Oxidative treatment of simulated dye house effluent UV and near-UV light-assisted Fenton's reagent, Chemosphere 39:2767–2783.

Awad H. S., Galwa N. A., H. S., (2005). Elecrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO_2 electrode in the presence of different conductive electrolyte and effect of various operating factors. Chemosphere, 61:1327-1335.

Banat I. M., Nigam P., Mcmullan G., Marchant R., Singh D., (1997). The isolation of thermophilic bacterial cultures capable of textile dyes decolourisation. Environment International, 23:547-551.

Barr D. P., Aust S. D., (1994). Mechanisms white rod fungi use to degrade pollutants. Environmental Science & Technology, 28:320-328.

Bastaki N., (2004). Removal of methyl orange dye and Na_2SO_4 salt from synthetic waste water using reverse osmosis. Chemical Engineering & Processing, 43:1561-1567.

Baughman G.L., Perenich T.A., (1988). Fate of dyes in aquatic systems: Solubility and partitioning of some hydrophobic dyes and related compounds. Environmental Toxicology Chemistry, 7:183-199.

Catalkaya E.C., Sengul F., (2005). Application of Box-Wilson experimental design method for the photo degradation of bakery's yeast industry with UV/H_2O_2 and UV/H_2O_2/Fe(II) process, Journal of Hazardous Materials, 128:201-207.

Chaco J.M., Leal M.T., Sanchez M., Bandala E.R., (2006). Solar photocatalytic degradation of azo-dyes by photo-Fenton process, Dyes and Pigments 69:44-150.

Chacon J.M., Leal M.T., Sanchez M., Bandala E.R., (2006). Solar photocatalytic degradation of azo dyes by photo-Fenton process. Dyes and Pigments 69:144-50.

Chaudhuri S.K., Sur B., (2000). Oxidative decolorization of Reactive Dye Solution using Fly Ash as Catalyst, Journal of Environmental Engineering, 583.

Chen H., (2006). Recent advances in azo dye degrading enzyme research. Current Protein-Peptide Science, 7:101-111.

Chung K.T, Stevens S.E.J., Cerniglia C.E., (1992). The reduction of azo dyes by the intestinal microflora. Critical Reviews in Microbiology 18:175-97.

Chung K.T., Stevens S.E.J., (1993). Degradation of azo dyes by environmental microorganisms and helminths. Environmental Toxicology and Chemistry 54:435-41.

Chung KT, Stevens SEJ, Cerniglia CE, (1992). The reduction of azo dyes by the intestinal microflora. Critical Reviews in Microbiology, 18:17-97.

Comisio n Ambiental Metropolitana., (1998). Manual de minimizacio n, tratamiento y disposicio n. Concepto de manejo de residues industriales para el giro textile.

Crini G., (2006). Nonconventional low cost adsorbents for dye removal: A review. Bioresource & Technology, 97, 1061-1085.

Das, (2000). Textile effluent treatment- A solution to the environmental pollution, drsubratadas2000@gmail.com.

Daud N.K., Hameed B.H., (2010). Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst Journal of Hazardous Materials 176:938–944.

De A.K., Chaudhuri B., Bhattacharjee S., Dutta B.K., (1999). Journal of Hazardous Materials B64, 91.

Devi L.G., Kumar S.G., Reddy K.M., Munikrishnappa C., (2009). Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism, Journal of Hazardous Materials 164:459–467.

Djeffal L., Abderrahmanea S., Benzinad M., Siffert S., Fourmentinb S., (2013). Efficiency of natural clay as heterogeneous Fenton and photo- Fenton catalyst for phenol and tyrosol degradation, Desalination and Water Treatment, 1–6.

Erden G., Filibeli A., (2010). Improving anaerobic biodegradability of biological sludges by Fenton pre-treatment: Effects on single stage and two-stage anaerobic digestion, Desalination 251:58–63.

Fatemeh R, Franklin W and Cerniglia C.E., (1990). Applied and Environmental Microbiology, 56:2146-2151.

Faust B.C., Hoigne J., (1990). Photolysis of Fe(II)-hydroxyl complexes as sources of OH radicals in clouds, fog and rain, Atmospheric Environment 24:79-89.

Feng J., Hu X., Yue P.L., Zhu H.Y., Lu G.Q., (2003). Discoloration and mineralization of Reactive Red HE-3B by heterogeneous photo- Fenton reaction. Water Research 37:3776-84.

Ferrero F., (2007). Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood saw-dust. Journal of Hazardous Materials, 142:144-152.

Gahr F., Hermanutz F., (1994). Ozonation- an important technique to comply with new German law for textile waste water treatment. Water Science& Technology, 30, 255-263.

Golob V., Vinder A., Simonic M., (2005). Efficiency of the coagulation/ flocculation method for the treatment of dye bath effluents. Dyes & Pigments, 67, 93-97.

Guimaraes B., Kleemann N., Caldas S., Costa F., Silveira M., (2013). Environmentally friendly system for the degradation of multipesticide residues in aqueous media by the Fenton's reaction Environmental Science and Pollution Research 11356-013-1932-2.

Gupta V.K., Suhas, (2009). Application of low-cost adsorbents for dye removal e a review. Journal of Environmental Management 90:2313-2342.

Hameed B.H., Ahmad A.L., Latiff K.N.A., (2007). Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes Pigment 75:143–149.

Hao O.J., Kim H., Chiang P.C., (2000). Decolorization of wastewater, Environmental Science and Technology.

Hsueh C.L., Huang Y.H., Wang C.C., Chen S., (2005). Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere 58:1409.

Huang C.P., Huang Y.H., (2009). Application of an active immobilized iron oxide with catalytic H_2O_2 for the mineralization of phenol in a batch photo-fluidized bed reactor, Applied Catalysis A 357:135–141.

Huitle C.A., Brillas E., (2009). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review, Applied Catalysis B 87: 105–145.

Karcher S.A., (2001). Screening of commercial sorbents for the removal of reactive dyes. Dyes Pigments 51:111-25.

Karimi S., Abdulkhani A., Ghazali A.H.B., Ahmadun F.R., Karimi A., (2009). Color remediation of chemimechanical pulping effluent using combination of enzymatic treatment and Fenton reaction, Desalination 249:870–877.

Katsumata H., Sada M., Kaneco S., Suzuki T., Ohta K., Yobiko Y., (2008). Chemical Engineering Journal 137, 225.

Khadhraoui M., Trabelsi H., Ksibi M., Bouguerra S., Elleuch B., (2009). Discolouration and detoxification of a congo red dye solution by means of ozone treatment for a possible water reuse. Journal of Hazardous Materials, 161, 974-981.

Kitis M., Kalpana M.M., (2007). Advanced oxidation of natural organic matter using hydrogen peroxide and iron-coated pumice particles. Chemosphere 68:1846-1853.

Kouba J.F., Zhuang P., (1994). Color removal for textile dyeing wastewater. Journal of fluids engineering 7(3):87-90.

Kuo WG., (1992). Decolorizing dye wastewater with Fenton's reagent. Water Research 26(7):881-6.

Lars B.R., Mallika I., (1997). Optimization of Reactive Black 5 dye and Reactive Red 120 dye degradation Chemosphere, 35:585-597.

Legrini O., Oliveros E., Braun A.M., (1993). Photochemical processes for water treatment. Chemical Reviews 93:671-98.

Liakou S., Pavlou S., Lyberatos G., (1997). Ozonation of azo dyes. Water Science and Technology 35(4):279-86.

Liang J., Komarov S., Hayashi N., Kasai E., (2007). Degradation of chlorophenols using ultrasound. Ultrasonics Sonochemistry 14:201.

Liao Q., Sun J., Gao L., (2009). Degradation of phenol by heterogeneous Fenton reaction using multi-walled carbon nanotube supported Fe_2O_3 catalysts, Colloids and Surfaces A 345:95–100.

Liotta L.F., Gruttadauria M., Carlo G.D., Perrini G., Librando V., (2009). Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity, Journal of Hazardous Materials 162 :588–606.

Lipczynska-Kochany E., (1991). Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction. Chemosphere 22(5-6):529-36.

Lodha B., Chaudhari S., (2007). Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solution. Journal of Hazardous Materials, 148:459-466.

Lucas M.S., Peres J.A., (2006). Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes and Pigments 71:236-244.

Madhavan J., Grieser F., Kumar M.A., (2010). Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments, Journal of Hazardous Materials 178:202-208.

Mahmoodi N. M., Arami M., (2009). Degradation and toxicity reduction of textile waste water using immobilized titania nano photocatalysis. Journal of Photochemistry & Photobiology B : Biology, 94:20-24.

Mandal T., Maity S., Dasgupta D., Datta S., (2010). Advanced oxidation process and biotreatment: Their roles in combined industrial wastewater treatment, Desalination 250:87–94.

Martinez F., Calleja G., MeleroJ.A., Molina R.,(2005). Heterogeneous photo-Fenton degradation of phenolic aqueous solutions over iron-containing SBA-15 catalyst, Environmental 60: 181–190.

Mass R., Chaudhari S., (2005). Adsorption and biological decolorization of azo dye Reactive Red-2 in semi continuous anaerobic reactors, Process Biochemistry, 40:699–705.

Mathur N., Bhatnagar P., (2007). Mutagenicity assessment of textile dyes from Sangner(Rajasthan). Journal of Environmental Biology, 28:123-126.

Medvedev Z. A., Crowne H. M., Medvedeva M. N., (1988). Age related variations of hepato carcinogenic effect of azo dye (3’- MDAB) as linked to the level of hepatocyte polyploidization. Mechanisms of Ageing Devlopement, 46:159-174.

Meric S., Kaptan D., lmez T., (2004). Color and COD removal from wastewater containing Reactive Black 5 using Fenton’s oxidation process. Chemosphere 54:435-41.

Meunier L., Canonica S., U. von Gunten. (2006). Implications of sequential use of UV and ozone for drinking water quality” Water Research 40:1864- 1876.

Modirshala N., Behnajady M.A., Ghanbary F., (2007). Decolorization and mineralization of C.I. acid yellow 23 by Fenton and photo-Fenton processes, Dye Pigments 73:305-310.

Mok L.S., Diwakar T., (2009). Application of ferrate(VI) in the treatment of industrial wastes containing metal-complexed cyanides: A green treatment, Journal Environmental Science 21:1347–1352.

Neamtu M., Yediler A., Siminiceanu I., Kettrup A., (2001). Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. Journal of Photochemistry and Photobiology A: Chemistry 141:247-54.

Nigam P., Armour G., Banat I. M., Singh D., Marchant R., (2000). Physical removal of textile dyes and solid state fermentation of dye adsorbed agricultural residues. Bioresource & Technology, 72:219-226.

Nigam P., Armour G., Banat I.M., Singh D., Marchant R., (2000). Physical removal of textile dyes and solid state fermentation of dye-adsorbed agricultural residues. Bioresource & Technology 72:219–226.

Pandey A., Singh P., Iyengar L., (2007). Bacterial decolorization and degradation of azo dyes. International Biodeterioration & Biodegradation 59:73–84.

Park H., Choi W., (2003). Visible light and Fe(III)-mediated degradation of Acid Orange in the absence of H_2O_2. Journal of Photochemistry and Photobiology A: Chemistry ,159:241-7.

Percy A. J., Moore N., Chipman J. K., (1989). Formation of nuclear anomalies in rat intestine by benzidine and its biliary metabolites. Toxicology, 57:217-223.

Perez M., Torrades F., Garcia-Hortal J.A., Domenech X., Peral J., (2002).Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Applied Catalysis B 36:63–74.

Quan X., Zhang Y., Chen S., Zhao Y., Yang F., (2007). Generation of hydroxyl radical in aqueous solution by microwave energy using activated carbon as catalyst and its potential in removal of persistent organic substances, Journal of Molecular Catalysis Chemistry 263:216–222.

Raquel O.C., Tavares A.P.M., Ribeiro A.S., Loureiro J.M., Boaventura R.A.R., MacedoE.A., (2008). Kinetic modelling and simulation of laccase catalyzed degradation of reactive textile dyes, Bioresource Technology 99:4768–4774.

Rauf M.A., Ashraf S.S., (2009). Radiation induced degradation of dyes — an overview, Journal of Hazardous Materials 166:6–16.

Reactive Red HE-3B by heterogeneous photo-Fenton reaction. *Water Research*.37:3776-3784.

Reife A., Freeman H.S., (1996). Environmental chemistry of dyes and pigments. New York: Wiley/Interscience. removal of atrazine, Chemosphere 51:305–311.

Samanta C., (2008). Direct synthesis of hydrogen peroxide from hydrogen and oxygen: An overview of recent developments in the process, Applied Catalysis A 350:133–149.

Sarasa J., Roche M.P., Ormad M.P., Gimeno E., Puig A., Ovelleiro J.L., (1998). Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. Water Research 32(9):2721-7.

Slokar Y. M., Le Marechal A. M., (1997). Methods of decolouration of textile waste waters. Dyes & Pigments, 37:335-356.

Song Y.L., Ji-Tai Li. (2009). Degradation of C.I. Direct Black 168 from aqueous solution by fly ash/H_2O_2 combining ultrasound. Ultrasonics Sonochemistry 16: 440–444.

Sun J.H., Sun S.P., Wang G.L., Qiao L.P., (2008). Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process, Dyes Pigment 74:647–652.

Tanaka K., Padermpole K., Hisanaga T., (2000). Photocatalytic degradation of commercial azo dyes, Water Research 34:327–333.

Tang H., (1990). Basic researches on inorganic polymer flocculant. Environmental Chemistry, 10:1-12.

Tanja K., Alenka M., Marcechal L., Darinka B. V., (2003). Comparision of H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes for the decolourisation vinyl sulphone reactive dyes. Dyes & Pigments, 58:245-252.

Tony M.A., Zhao Y.Q., Fu J.F., Tayeb A.M., (2008). Conditioning of aluminium-based water treatment sludge with Fenton's reagent: effectiveness and optimizing study to improve dewaterability. Chemosphere. Jun;72(4):673-7.

Torrades F., Saiz S., Garcia-Hortal J.A., Garcia-Montano J., (2007). Environmental Engineering Science 25, 92.

Torres L.G., Jaimes J., Mijaylova P., Ramrez E., Jimenez B., (1997). Coagulatione flocculation pretreatment of high-load chemicalepharmaceutical industry wastewater: mixing aspects.Water Science & Technology 36(2/3):255-62.

Torres R.A., Abdelmalek F., Combet E., Petrier C., Pulgarin C., (2007). Journal of Hazardous Materials B146.

Umbuzeiro G.A., Freeman H.S., Warren S.H., Oliveira D.P., Terao, Y., Watanabe T., Claxton D. L., (2005). The contribution of azo dyes to the mutagenic activity of Cristais river. Chemosphere, 60:55-64.

Vandevivere P.C., Bianchi R., Verstraete W., (1998). Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. Journal of Chemical Technology and Biotechnology 72:289–302.

Vogel E.W., (1982). Assessment of Chemically Induced Genotoxic Events, Prospectives and Limitations, vol. 2:24, Universitaire Pers Leiden, Leiden, The Netherlands.

Walling C., (1998). Intermediates in the reactions of Fenton type reagents. Accounts of Chemical Research 31(4):155-7.

Wang C. X., Yediler A., Lienert D., Z. J. Wang, A. Kettrup, (2002). Toxicity evaluation of reactive dye stuffs, oxilaries and selected effluents in textile finishing industry to luminescent bacteria vibrio fischeri. Chemosphere, 46:339-344.

Wang K. S., Chen H. Y., Huang L. C., Su Y. C., Chang S. H., (2008). Degradation of Reactive Black 5 using combined electrochemical degradation- solar- light/immobilized TiO_2 film process and toxicity evaluation. Chemosphere, 72:299-305.

Wang K.S., Chen H.Y., Huang L.C., Su Y.C., Chang S.H., (2008). "Degradation of Reactive Black 5 using combined electrochemical degradation-solar-light/immobilized TiO_2 film process and toxicity evalution", Chemosphere, 72:299.

Weber E., Wolfe N.L., (1987). Kinetic studies of reduction of aromatic azo compounds in anaerobic sediment/water systems. Environmental Toxicology Chemistry, 6:911-920.

Wojnarovits L., Takacs E., (2008). Irradiation treatment of azo dye containing wastewater: An overview, Radiation Physics and Chemistry 77:225–244.

Yoshida Y., Ogata S., Nakamatsu S., Shimamune T., Kikawa K., Inoue H., (1999). Decolorization of azo dye using atomic hydrogen permeating through a Pt-modified palladized Pd sheet electrode, Electrochimica Acta 45:409–414.

Zee F. P., Villaverde S., (2005). Combined anaerobic- aerobic treatment of azo dyes-a short review of bio-reactor studies, Water Research, 39(8):1425-1440.

Zee F.P., (2002). Anaerobic azo dye reduction. Doctoral thesis. Wageningen, The Netherlands: Wageningen University,142.

Zhu M. Xu., Lee L., Wang H. H., Wang Z., (2007). Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud. Journal of Hazardous Materials, 149:735-741.