Heterogeneous photocatalytic (slurry and immobilized) and photo-Fenton (using Foundry Sand) degradation studies of 2-Chloro-4-nitrophenol

A Dissertation

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Masters of Technology
in
Environmental Science and Technology

Submitted
By

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July 2015

CERTIFICATE

This is to certify that thesis entitled, **"Heterogeneous photocatalytic (slurry and immobilized) and photo-Fenton (using Foundry Sand) degradation studies of 2-Chloro-4-nitrophenol"** submitted by **Ms. Kashish Aggarwal** in partial fulfillment of the requirements for the award of **Masters of Technology** Degree in **Environmental Science and 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 any degree or diploma.

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DECLARATION

I hereby declare that the research work presented in thesis entitled, **"Heterogeneous photocatalytic (slurry and immobilized) and photo-Fenton (using Foundry Sand) degradation studies of 2-Chloro-4-nitrophenol"** is original piece of work and was carried out under the supervision and guidance of **Dr. Anoop Verma, Assistant Professor, Thapar University, Patiala.**

Further, I declare that the matter presented in this thesis has not been submitted in part or full to any other University/Institute for any degree or diploma.

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Kashish Aggarwal

ABSTRACT

The present study deals with degradation and mineralization of 2Cl4NP through advanced oxidation processes (AOPs) including heterogeneous photocatalysis with suspended and supported TiO_2 and heterogeneous solar photo-Fenton process. In heterogeneous slurry photocatalysis the effect of different operating parameters like amount of catalyst, oxidant, pH, A/V ratio and UV intensity were studied whereas effect of foundry sand concentration, oxidant addition as well as iron leaching were studied in solar photo-Fenton process for the degradation of 2Cl4NP. Cement and clay beads were prepared as support materials for TiO_2 immobilization for studying fixed-bed photocatalytic degradation of 2Cl4NP. Foundry Sand (FS) was used as an alternate iron source in heterogeneous solar photo-Fenton process as SEM-EDS analysis of FS showed the presence of iron in sufficient amount to act as a catalyst in the degradation process. Degradation of 2Cl4NP was analyzed through UV-Visible spectrophotometer at 266 nm and HPLC. In slurry photocatalysis, 97.19% degradation of 2Cl4NP was achieved in 210 min at optimized conditions of C_0=50 mgL^{-1}, pH=4, 0.15 g TiO_2 and H_2O_2= 0.1 mL. The degradation of 68% and 52% of 2Cl4NP was attained in fixed-bed photocatalysis using cement and clay beads respectively and efficacy of cement and clay beads was checked and durability studies of cement and clay beads were carried out. In heterogeneous solar photo-Fenton process 97.19% degradation was obtained in 105 min at optimized conditions of FS= 0.1 g, H_2O_2=0.05 mL and pH=3. Complete mineralization of 2Cl4NP was confirmed through reduction in COD along with the disappearance of parent compound peak in HPLC chromatograms.

Keywords:- Heterogenous photocatalysis; Immobilization; Solar photo-Fenton; 2-Chloro-4-nitrophenol

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CHAPTER 1

INTRODUCTION

Nations and individuals are facing a wide range of water problems around the world. These problems include water scarcity, contamination, international and regional disputes over water, unsustainable use of groundwater, ecological degradation. Because of these water problems billions of people are not provided even with the basic water services resulting in damaging of human health **(Gleick, 2002).**

The United Nations collaborates with individual nations to regularly monitor access to water and sanitation. In wealthier nations water related diseases have largely been controlled but they are a main concern in much of the developing world. According to assessment published by WHO in 2000, 1.1 billion people around the world lacked access to improved water supply and more than 2.4 billion lacked access to improved sanitation. WHO also estimated that there are four billion cases of diarrhea each year in addition to millions of other cases of illness associated with the lack of access to clean water. The right amount of these diseases is unknown as number of illness is not diagnosed **(Gleick, 2002).**

Water related diseases include:

1. Water-borne (bacteria, fecal contamination)
2. Water-based (toxic material)
3. Water-related vectors and water-scarce diseases.

The first two are mostly related with lack of improved domestic water supply.

Water-borne diseases include: dysentry, diarrhea, cholera, typhoid, hepatitis and polio. Water-related vector diseases include: malaria and dengue **(Villen et al., 2006).**

50% of the population in developing countries, are exposed to polluted water sources which includes water for personal hygiene and sanitation, are the main contributors for estimated 4 billion cases of diarrhea each year. These result in an estimated 2.2 million deaths each year, the majority of which are children under the age of five (**Clasen and Edmondson, 2006).**

The Millennium Development Goal (MDG) drinking water target, which calls for halving the proportion of the population without sustainable access to safe drinking water between 1990 and 2015, was met in 2010, five years ahead of schedule. Despite the fact that this is a great achievement, continued efforts are needed as, in 2012, 748 million people still relied on unimproved drinking water sources, 2.5 billion people still lacked access to improved sanitation facilities, 1 billion people practiced open defecation **(Global Health Observatory (GHO) data, WHO).**

Surface and groundwater contamination are mainly because of excessive use of pesticides, industrial effluents (even in small amounts), fertilizers (agrochemicals) and domestic waste landfills, pharmaceutical wastes **(Malato et al., 2007).** Stability of these materials to natural decomposition, toxicity and their persistence in the environment are the main cause of concern to the society. Even though the hazardous organic wastes present in water resources is the outcome of different industries , the pesticide industry and the pharmaceutical industry is of major concern **(Chiron et al., 2000).**

Pharmaceutical compounds have been observed in surface water **(Kolpin et al., 2002; Anderson et al., 2004; Rabiet et al., 2006)**, ground water (**Rabiet et al., 2006)**, sewage effluent **(Carballa et al., 2004; Nikolaou et al., 2007)** and even in drinking water (**Stackelberg et al., 2004)**. They are mainly concerned because of their permanent effects on terrestrial and aquatic environment. Pharmaceutical compounds can reach the aquatic environment through various sources such as hospital effluent, pharmaceutical industry and excretion from humans and livestock (**Nikolaou et al., 2007; Ikehata et al., 2006; Yang et al., 2008).**

Pesticides are world-wide used for agricultural and domestic protection of plants, woods, soils, and to control the growth of certain vegetation. Although there are many advantages of pesticides, but some can badly affect the human health and environment **(Konstantinou et al., 2001).** Many pesticides leach down to sub soil and contaminate the ground water and if they are immobile they could stay on the top soil and become harmful to animals, plants and humans **(Jha and Mishra, 2005; Radivojević et al., 2008**). Increased levels of pesticides in water system can deteriorate the quality of water and make it unfit for human consumption **(Konstantinou et al., 2001).**

Biomagnification of pharmaceutical and pesticide compounds is reported hence it is necessary to apply the appropriate treatment. Conventional methods includes the biological processes, filtration and coagulation/flocculation/ sedimentation **(Adams et al., 2002; Göbel et al., 2007; Stackelberg et al., 2007; Vieno et al., 2007; Arikan, 2008).** These conventional methods are capable of breaking the organic matter but will convert them from one form to other form as a result problem will persist in one form or the other.

It is clear from the above discussion that pesticide and pharmaceutical industries generate large amount of toxic waste which contains hazardous and complex compounds. The characteristics of the waste from both industries proves that conventional treatment methods are not able to degrade the complex compounds which are stable, non-biodegradable, hence advanced treatments are required either in conjugation with conventional treatments or individually.

In recent years, one of the advanced treatment technology picking up the pace is photocatalysis with TiO_2, is a clean, low cost water treatment technology which can offer additional advantages in wide range of applications **(Herrmann, 2005)**. Suitable band gap semiconductor material such as TiO_2 is used in this process to generate the reactive oxygen species (ROS). Addition of chemical consumables is not required and they don't produce hazardous waste products **(Duffy et al., 2004; Gelover et al., 2006).**

TiO_2 is used for the treatment of different types of water contamination **(Herrmann et al., 1998).** Photocatalytic reaction (fig. 1) that generates electron-hole pairs on the semiconductor surface takes place when TiO_2 is excited by the energy of near UV-radiation (<400nm) **(Herrmann, 2005).** In the presence of water and oxygen, hydroxyl radicals (OH) are formed **(Hoffmann et al., 1995).** Hydroxyl radicals are known to be strong, not very selective oxidizing agents. The principal reaction mechanism includes following reactions (**Wang and Hong, 1999)**.

$$TiO_{2} + \text{light} \longrightarrow h_{TiO2}^{+} + e_{TiO2}^{-} \tag{1}$$

$$h_{TiO2}^{+} + H_2O \longrightarrow {}^{\cdot}OH_{TiO2}^{+} + H^{+} \tag{2}$$

$$e_{TiO2}^{-} + O_2 \longrightarrow O_{2,TiO2}^{-} \tag{3}$$

$$O_{2,TiO2}^{-} + e_{TiO2}^{-} \longrightarrow O_2^{2-} \tag{4}$$

$$O_2^{2-} + H^{+} \longrightarrow HO_2 \tag{5}$$

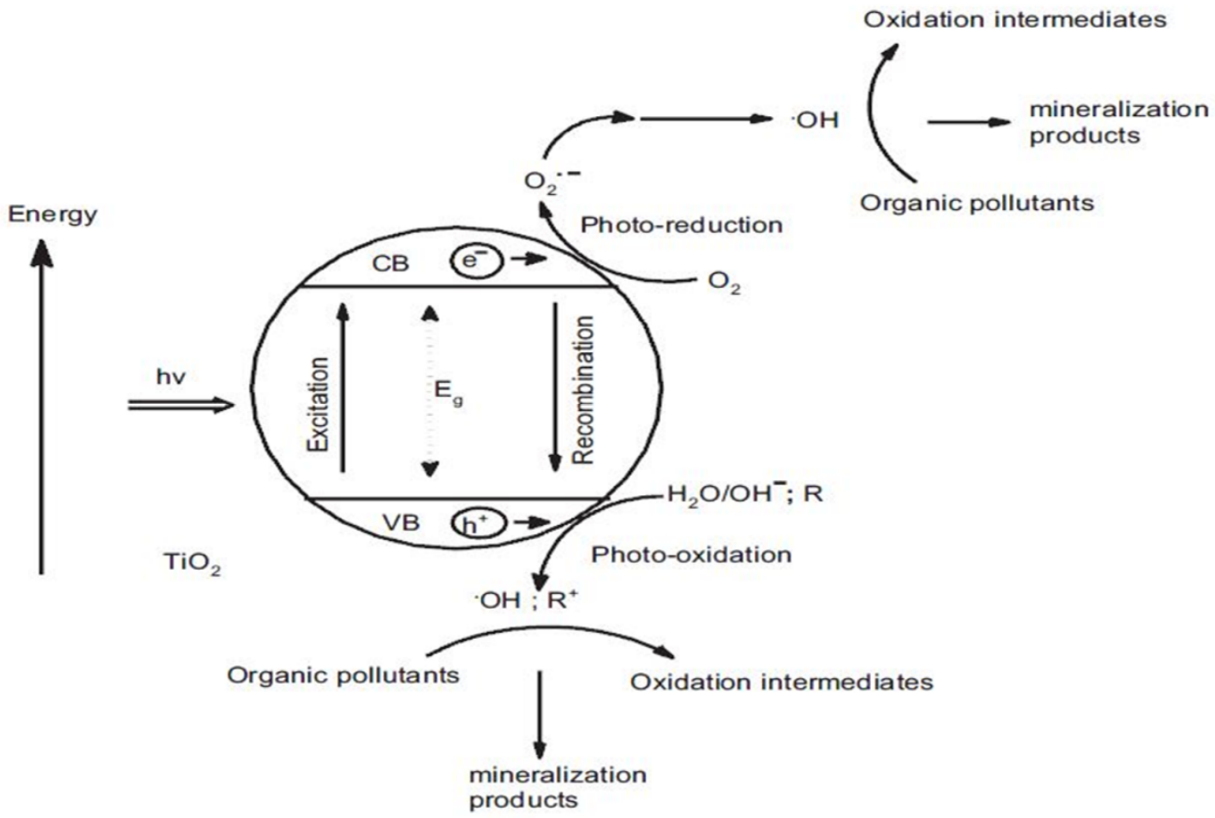

Figure 1: Photocatalytic mechanism of TiO_2.

The process of TiO_2 photocatalysis can be employed both in the slurry or suspension and fixed form. The application of TiO_2 in suspension form is efficient because large surface area of catalyst is available for the reaction. However, there are a number of disadvantages from practical and economical point of view, as the catalyst particles needs to be removed after the treatment **(Gurr et al., 2005).** Alternatively, the catalyst may be immobilized onto an appropriate solid support which eliminates the need of post treatment removal, but the main disadvantage associated with it is the decrease in the surface area available for catalytic reaction **(Robert et al., 1999).**

Another type of AOP is the homogeneous photocatalysis (photo-Fenton) which react up to a light wavelength of 600 nm. This technique was recognized in the 1960s and is one of the most applied AOPs because it has ability to degrade high loading of organic compounds in highly saline conditions **(Neyens and Baeyens, 2003).**

The photo-Fenton reaction speeds up when light source is present which causes fast decomposition of H_2O_2 by ferrous or ferric ions and results in the formation of radicals as shown in fig.2. When ferrous sulphate is added to H_2O_2 solution in Fenton systems, reaction that leads to the formation of hydroxyl radical ($OH^{\cdot}$) and various other competing reactions occur. The production of hydroperoxyl radicals, the cycling of iron (III) to iron (II) and the quenching of $OH^{\cdot}$ by iron (II) and H_2O_2 occur, as summarized in following reactions **(Mohanty and Wei, 1993).**

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH^{\cdot} \quad (6)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^{+} + HO_2^{\cdot} \quad (7)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+} \quad (8)$$

$$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (9)$$

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (10)$$

$$HO_2^{\cdot} + Fe^{2+} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \quad (11)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (12)$$

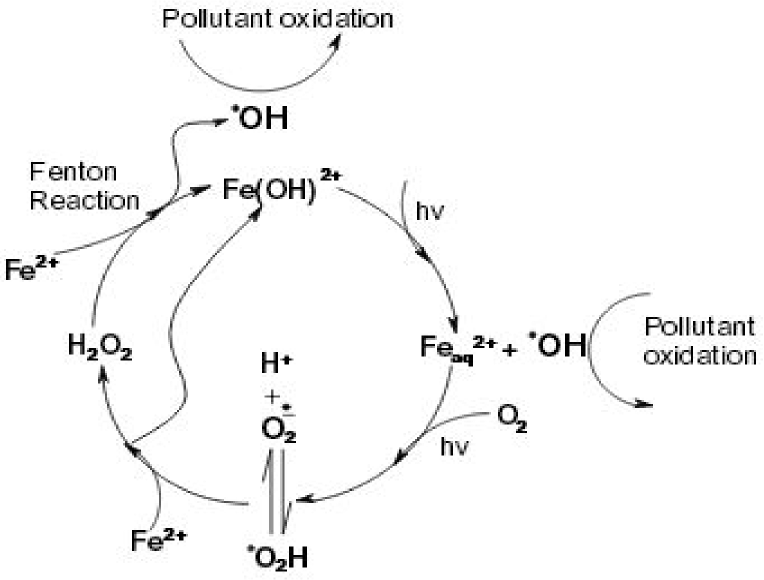

Figure 2: Model of photo-assisted Fenton System.

In this reaction, there is no mass transfer limitations because of its homogeneous catalytic nature, there is no energy involved as catalyst and the process is easy to run and control also. Iron and H_2O_2 are cheap and non toxic **(Torrades et al., 2003).** Not only UV radiation but visible light is also absorbed by soluble iron-hydroxy or iron complexes. The generation of the highly photoactive iron complexes is highly dependent on the water pH and ions content **(De Laat et al., 2004).**

Though homogenous photocatalysis leads to higher removal rate **(Kwon et al., 1999)** but it has major disadvantage of removal of iron ions at the end of treatment which is quiet expensive and difficult. However in heterogeneous photo-Fenton process the catalyst is easily recovered either by filtration or sedimentation and can be used again. Different iron sources can be used as heterogeneous catalysts. Different iron oxides and iron powder have been tested **(Lucking et al., 1998).** Different substances that can be used as hetero-Fenton catalysts, include Fe-treated laponite, iron exchanged zeolite **(Tekbas et al., 2008),** iron loaded resin **(Cheng et al., 2007),** Fe_3O_4, Fe_2O_3 and S-doped Fe_2O_3 **(Feng et al., 2004).**

In our studies Foundry sand (FS) is used as alternative iron source. Foundry sand is a mixture of silica sand (80-95%), bentonite clay (4-10%), carbonaceous additive (2-10%) and water (2-5%). FS is a good source of iron, silica and alumina. FS is high quality silica which has uniform physical characteristics and is used for mould making. It is obtained from ferrous and non-ferrous metal casting industry as a byproduct. According to estimates 100 million tons of sand is used by industries in production annually. Every year foundries generate 9 to 13 million tons of sand which is unfit for continued use in 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 constitute a driving force for the adoption of novel methods for its reuse. As a result FS is used as alternative iron source in heterogeneous solar photo-Fenton process. FS is black in color and its chemical and physical properties depend on casting process, metal being poured, technology employed, type of furnance and type of finishing process (coating, grinding and blast cleaning).

2-Chloro-4-nitrophenol (2Cl4NP) is one of the compounds among those toxic and complex compounds. It is used as an intermediate in both the pesticide and pharmaceutical industry. If 2-Chloro-4-nitrophenol is ingested or absorbed through the skin or inhaled then it is harmful. The main effects are that it causes irritation to the skin, gastrointestinal tract, eyes and respiratory. It may also cause cyanosis. From above discussion it is clear that conventional methods are not sufficient to degrade non-biodegradable compounds like 2Cl4NP.

The present study investigates the photodegradation efficiency of various treatment technologies for the degradation of 2Cl4NP. Heterogeneous photocatalysis using suspended and supported TiO_2 both has been studied for the degradation of the selected compound (2Cl4NP). Various inert supports like cement beads and clay beads have been used for TiO_2 immobilization. Attempts have also been made to carry out the degradation of compound through heterogeneous solar photo-Fenton process using foundry sand as an alternative iron source.

CHAPTER 2
LITERATURE REVIEW

2.1 Overview

Presence of pharmaceutical compounds in surface waters is a rising environmental issue and it provides a new challenge to drinking water, wastewater and water reuse treatment systems (**Ikehata et al., 2006)**. The persistence of the residues of the pharmaceutical compounds in surface waters is of great concern because of their potential impact on public health and ecosystem **(Cleuvers, 2005; Sharma, 2008).** According to recent research reports **(Fernandez et al., 1998; Nakashima et al., 2002)** there is existence of insecticides, metabolites and herbicides, which are Endocrine disrupting chemicals (EDCs), in surface and ground water via point and non-point sources. These chemicals have been detected in reproductive tissue, blood and urine **(Guo et al., 1993; Keith, 1996; Ohko et al., 2002).** These chemicals have serious effects on humans, which includes premature ageing, congenital abnormalities and impotence **(Keith, 1998; Ohko et al., 2002).** Different pollutants require different treatment technologies and techniques may be pollutant specific with different/variable efficiency towards different pollutants. Thus, the need of the hour is the development of hybrid technologies or new advanced treatment technologies so as to achieve the goal of pollution free environment and decontaminated water.

2.2 Conventional Techniques vs. Advanced Techniques

Conventional waste water purification techniques include activated carbon adsorption, chemical oxidation, membrane filtration, ion exchange on synthetic adsorbent resins, oxidation, biological treatment etc. During the treatment of contaminated water these techniques generate wastes that require additional steps and cost **(Ahmed et al., 2010)**. Pollutants get transferred from one phase to another without decomposition during activated carbon adsorption and induce another pollution problem **(Juan, 1984).** Chemical oxidation is not capable of mineralizing all organic substances and is economically suitable only for the removal of pollutants at high concentrations **(Moza et al., 1988).** The main limitations of biological treatment are sludge disposal, slow reaction rates and the need for strict control of proper pH and temperature **(Haggblom, 1988; Dorn, 1988).**

Persistant organic pollutants (POPs) (example pesticides) are not effectively removed by conventional treatment technologies **(Bellobono et al., 1997).** They remain in environment for longer period of time**.** Moreover these techniques are not capable of treating water contaminated with pesticides from manufacturing and formulating industries. If problem persist after conventional treatment then ultimately human beings are the one who are affected which calls for modifications in conventional technologies or introduction of new techniques that prove their worth. Modifications in conventional technology such as adsorption, use of incinerators, and oxidation with peroxide or ozone are also not efficient for lower concentrations of organic pollutants **(Shankar et al., 2004).**

Then advanced techniques came into existence which includes Ozonation. Ozonation involves dark oxidation method used for the removal of emerging pollutants. In literature approximately 90% of the dark oxidation treatments correspond to Ozonation. More than 90% removal is achieved for numerous compounds, such as, pesticides, antibiotics, anti inflammatories, and natural and synthetic estrogens. The main disadvantages associated with Ozonation are that some compounds like clofibric acid, X-ray contrast agents are more recalcitrant to oxidation. Also low mineralization of micropollutants is achieved or we can say TOC removal is not very high **(Esplugas et al., 2007).** Supplying and production of ozone is also costly.

Still problems persist and we have to search for hybrid techniques or newer advanced oxidation technologies (AOT). Photocatalytic oxidation using semiconductor is emerging as one of the promising environment- friendly technique for the deduction of trace organic pollutants, in water.

In photocatalytic processes, TiO_2 semiconductor is commonly used which is chemically stable, economical and can be repeatedly used without any significant loss in catalytic activity. Heterogeneous photocatalysis is an ecofriendly process, is safe, nonhazardous, and doesn’t generate any harmful byproducts. Much research has been done in the field of photocatalytic removal of organic, inorganic, and microbial pollutants **(Fujishima et al., 2000; Rincon and Pulgarin, 2005).**

TiO_2 is used in lab in the form of slurry or suspension. This process provides more catalyst surface area to volume ratio for better contact between pollutant and hydroxyl radical, but its major disadvantage is that catalyst must be separated, which may not be economical on a large scale. However if the catalyst is immobilized there is no need for post-treatment separation but it leads to decrease in surface area to volume ratio and mass transfer which reduces the degradation rate.

2.3 Use of TiO_2 in slurry form:

Wang et al., 1999 used suspended TiO_2 in specifically built jacketed cylindrical type reactor under UV-light of 365 nm for studying the possible degradation of mono-substituted phenols. Their aim was to study the effect of anion additives, pH and the influence of co-existing reactants competing for reaction. Mineralization studies were carried out to find the efficiency of the treatment. From experimental results, they found complete degradation of 0.1 mM substituted phenol in 2 h by using 7.5 g/l TiO_2, pH 3, and light intensity of 2.25 mW/cm. The reaction appeared to be first order reaction which followed Langmuir-Hinshelwood model. Considerable inhibition of reaction occurred at pH 3 but not at high pH in case of chloride ions and small inhibition occurred for nitrate ions at pH 3. Results were different for the experiments with individual species than for the co-existing 2-chloro and 2-nitrophenol. Mineralization studies showed that substitution in the phenol ring doesn’t have much effect on the reaction rate but, complete mineralization was not achieved even after 9 h.

Elmolla and Chaudhuri, 2010 studied the photocatalytic degradation of antibiotics like amoxicillin, ampicillin and cloxacillin by using TiO_2 in aqueous solution. H_2O_2 enhanced the rate of photocatalysis and was evaluated. According to results not much degradation was achieved by 300-min UVA irradiation and antibiotic degradation was greatly affected by pH. Pseudo-first order kinetics was followed by photocatalytic reactions and the corresponding rate constants (k) for amoxicillin, ampicillin and cloxacillin were 0.007, 0.003 and 0.029 min−1. Complete degradation of amoxicillin, ampicillin and cloxacillin was achieved in 30 min by adding H_2O_2 at ambient pH 5 and TiO2 1.0 g/L. Mineralization of sulphur, nitrogen and organic carbon was indicated by sulphate ($SO_4{}^{2-}$) , nitrate ($NO_3{}^{-}$), ammonia (NH_3) formation and dissolved organic carbon (DOC) removal respectively.

The photocatalytic degradation kinetics of three sulfa pharmaceuticals (sulfachlorpyridazine, sulfapyridine and sulfisoxazole) was investigated by **Yang et al., 2010** in aqueous solution and it was found that after 60 min of illumination drugs were efficiently degraded with a removal efficiencies of 85.2%, 92.5% and 85.0% respectively. The effect of various parameters on kinetic study was also investigated and it showed that with increase in dose of catalyst degradation rate also increased while adsorption is greatly affected by the initial pH and consequently the degradation of pharmaceuticals is affected and degradation rates show different trends in the pH between 3.0–11.0. With increase in substrate concentration the degradation rate decreased which indicates that reaction occurs on surface of the catalyst. The mineralization of sulfa pharmaceuticals was confirmed by conversion of sulfurs into $SO_4{}^{2-}$and nitrogens into NH_4^+. Small amount of NH_4^+ was produced for sulfachlorpyridazine as compared to other two compounds. These variations are because of molecular structure of substrate.

The effect of size of the TiO_2 particles was studied by **Xu et al., 1999** on the degradation of methylene blue (MB) using suspended aqueous solution. According to results, adsorbability and the adsorption rate of MB increased with decrease in TiO_2 particle size. As the TiO_2 particle size decreases especially less than 30 nm activity of TiO2 increases. With decrease in TiO_2 particle size the half-life of the photocatalytic degradation of MB also decreased. Also with decrease in size of particles the rate constant of the first order reaction (degradation of MB) increased. In suspended solution MB's initial degradation rate was higher as compared to fixed-bed model. If the need to separate the fine TiO_2 particles is solved, photoreactor using TiO_2 in suspended form can be applied to industries.

Konstantinou et al., 2001 reported the photocatalytic degradation under solar light using aqueous TiO_2 suspensions of compounds like s-triazine herbicides and organophosphorus insecticides. Among s-triazines, herbicides like atrazine, propazine, cyanazine, prometryne, and irgarol were tested and insecticides from the organophosphorus group were ethyl parathion, methyl parathion, ethyl bromophos, methyl bromophos, and diclofenthion. Photocatalytic degradation followed first-order reaction and was analyzed through gas chromatography. The degradation of compounds depends on the type and structure of the compound. The possible pathways for the generation of transformation products (TPs) include dealkylation, oxidation, and dechlorination for s-triazines and photohydrolysis and oxidation for organophosphates. GC-MS and solid-phase extraction techniques were used to identify the TPs of bromophos, irgarol and dichlofenthion and possible degradation paths were proposed which proved that triazines and organophosporus pesticides have similar degradation pathway.

Degradation of a dilute aqueous solution of 2-chlorophenol (2-CP) using TiO_2 in an annular photocatalytic reactor was reported by **Rideh et al., 1997**. To optimize the degradation process physical and chemical factors like concentration of 2-CP, pH, dissolved oxygen concentration, catalyst concentration, temperature, and absorbed light intensity were studied. Reaction rate is higher for the experiments, performed in the presence of electron scavengers such as metallic ions, than oxygen which is used alone. The results led to proposal of kinetic approach which states rate determining step is the reaction of $OH^{\cdot}$ radical. Proposed kinetic model was based on a Langmuir type adsorption which involves solvent and substrate competition assuming that further oxygen adsorption sites were different from those of 2-CP and the oxygen adsorption obeys the Freundlich isotherm. Pollutant disappearance rate on dissolved 2-CP concentration, absorbed light intensity and oxygen partial pressure is justified by this model.

2.4 Use of TiO_2 in immobilized form:

The photocatalytic oxidation of methylene blue (MB) was carried out using immobilized TiO_2. TiO_2 was immobilized on polystyrene beads (fig. 3) which are naturally buoyant and coating is done via thermal treatment procedure. Good stability and photocatalytic activity are characteristics shown by the beads. Photocatalytic process doesn’t degrade the polystyrene support confirmed by thermogravimetric analysis of the beads after the treatment. The catalyst could be reused for up to 10 successive runs. By pausing the pulsation the buoyant coated beads under gravitational action move towards the top from they can be collected. With increase both in the pulsing conditions and catalyst loading reaction rate increases (**Fabiyi and Skelton, 2000).**

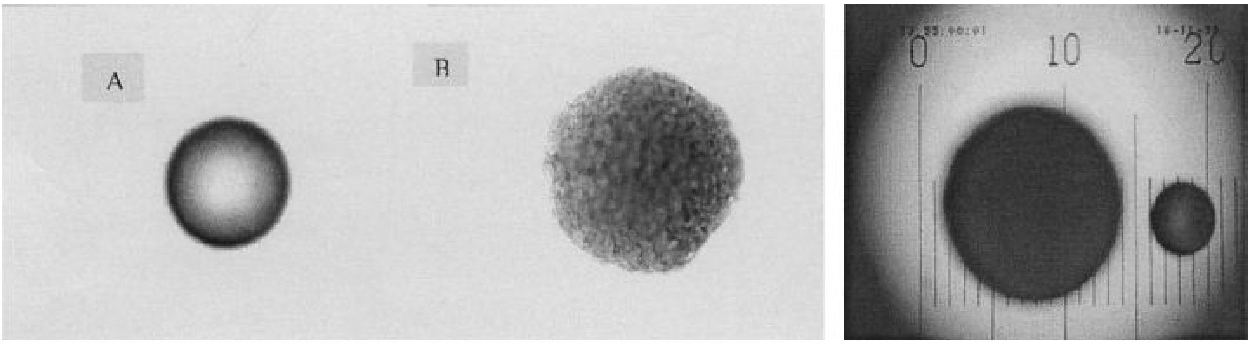

Figure 3: (a) Polystyrene beads: (A) Uncoated; (B) Coated Beads. (b) Relative sizes of the coated and un-coated beads (scale: 1 unit=100µm). Average particle diameter of un-coated beads is approx. 615µm.

To investigate the degradation of 4-chlorophenol, phenol, 2,4,5-trichlorophenol and 2,4-dichlorophenol over TiO_2, **Al-Ekabi and Serpone, 1988,** used three different photochemical reactors. TiO_2 was coated on internal surface of glass coil or external surface of glass beads of the reactors. Degradation of the phenolic compounds followed first-order kinetics. The reactors worked in a continuous recirculation mode.

Mozia et al., 2007 investigated the degradation of azo dye Acid Red 18 in water using immobilized TiO_2 in the quartz labyrinth flow reactor. Initial concentration of dye affected its decomposition rate. The reaction rate constants for dye concentrations of 10 and 30 mg/dm^3 came out to be 0.228 and 0.176 h^{-1}, respectively. Proposed system not only helped in decolorization but also in mineralization. After decolorization, 98% of TOC was vanished when the 10 mg/dm^3 solution was used and 99% when 30 mg/dm^3 used.

TiO_2 was immobilized on thin film reactor and was used for the degradation of pesticides like monocrotophos (MCP), 2,4-dichlorophenoxyacetic acid (DPA) and products formed from them in aqueous solution. Support materials like zeolites HY and Hβ having different physico-chemical properties were used. Immobilized TiO_2 showed greater degradation efficiency as compared to bare TiO_2. Technical grade pesticides took more time to mineralize as compared to formulated pesticides. The results confirmed the good adsorption capacity of the support and stability of supported photocatalysts was proved by reusability **(Shankar et al., 2004).**

Nogueira et al., 1996 studied the photocatalytic degradation of Dichloroacetic acid (DCA) using TiO_2 (Degussa P25) immobilized on a glass plate on a bench scale using sunlight as light source as shown in fig. 4. The influence of various parameters like solar light intensity, plate slope, flow rate and geometry of the reactor was looked upon. DCA gets mineralized into chloride ions. In 2 min of exposure to light, initial concentration of 5 mmol/L of DCA decayed to 2 mmol/L.

Table 1: Design Discussion of the fixed bed solar reactor

Supporting Material	Glass Plate
Area of Reactor	0.48 m^2
Flow Rate	2-6 l/min

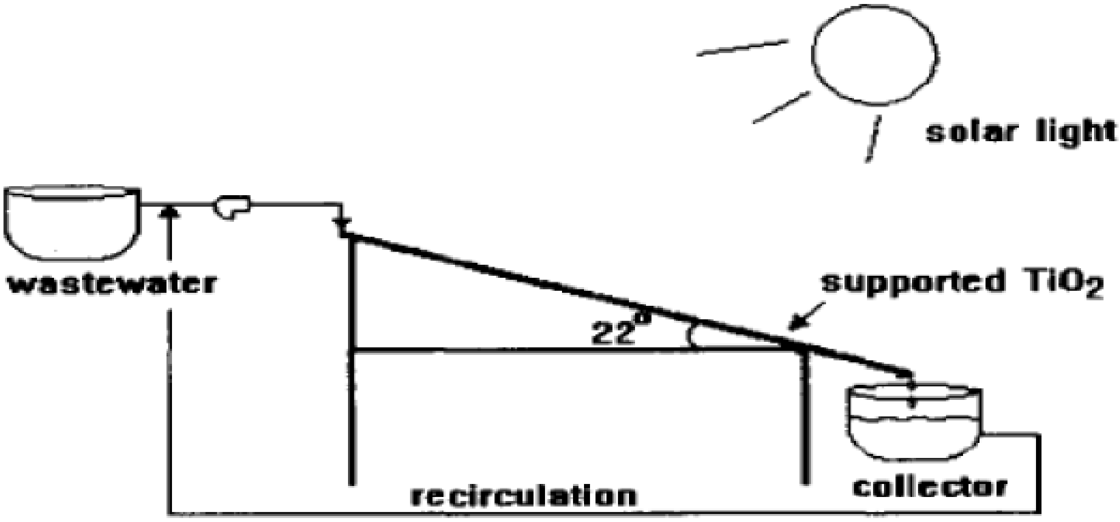

Figure 4: TiO_2 fixed bed solar reactor.

Noorjahan et al., 2003 performed experiments for the degradation of H-acid which is non-biodegradable and toxic dye intermediate. They performed experiments using both TiO_2 suspensions and TiO_2 thin film fixed bed reactor (TFFBR). TFFBR is shown in fig. 5. This method is useful as it avoids post-filtration process. Results show that 62% of COD removal occurred and at the end of third day BOD increased. TiO_2 is immobilized immobilization using an acrylic emulsion by simple spray technique on inert Cuddapah stone. Catalyst doesn’t require thermal treatment at higher temperature in this process. This method can be used at higher scale for photocatalytic treatment.

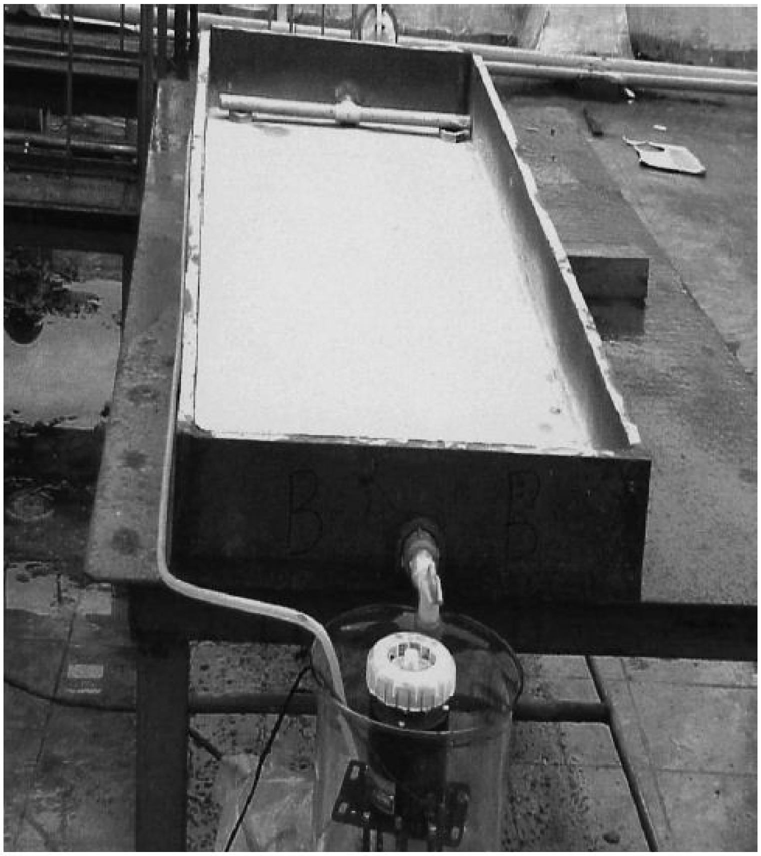

Figure 5: Photograph of TiO_2 TFFBR. Size 144cm× 52cm ×10cm.

Table 2: Design Discussion of Thin film fixed bed reactor

Supporting material used	Cuddapah stone
Size of the reactor	144cm*52cm*10cm
Flow rate	750 ml min^{-1}

Commercial azo dye was used to study the solar pilot plant for photocatalysis. To find out parameters affecting the functioning of the thin-film fixed-bed reactor (TFFBR) having an area of 25 m^2 (fig. 6), various experiments were performed. The results showed kinetic dependency on flow rate, catalyst loading, and initial dye concentration **(Zayani et al., 2009).**

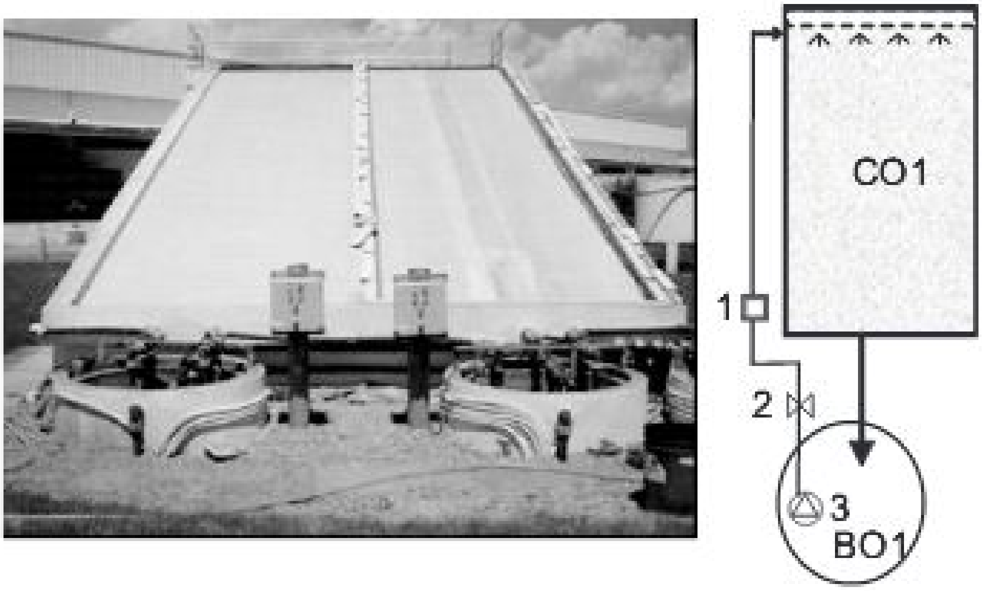

Figure 6: Photo and Simplified flow chart of TFFBR, (Recycling mode); (1, Flow Sensor, 2, Electrovalve, 3, pump).

Tennakone et al., 1995 immobilized TiO_2 on polythene films without affecting its photocatalytic activity. Generation of extra carbon dioxide may be due to partial degradation of the film or due to impurities in the film. Results show that almost 50% of phenol degraded in 2.5 h.

2.5 Degradation of persistent organic pollutants using photo-Fenton process

Fenton system was used to study the degradation of phenolic compounds like 2-chlorophenol, phenol and 2-nitrophenol using chlorides and sulfates. Degradation was affected by the presence of anions which may be because of radical ion generation reduction caused by the development of much less reactive inorganic radicals and iron complexes **(Siedlecka and Stepnowski, 2005).**

Oller et al., 2006 treated wastewater infected by six medium to highly soluble pesticides (methomyl, cymoxanil, dimethoate, oxamyl, telone and pyrimethanil) by TiO_2 photocatalysis and photo-Fenton process. Photo-Fenton treatment gave better results than TiO_2 proving its efficiency, not only for pesticide degradation, but also for TOC mineralization, except for dimethoate for which the mineralization rate was quite similar in both photocatalyitic treatments. For highest TOC removal time required for 20 mg L^{-1} of Fe^{2+} is always less (between20 times for telone and 1.5 times for dimethoate) than 200 mg L^{-1} of TiO_2.

For the treatment of different pesticides like atrazine, alachlor, isoproturon, pentachlorophenol, chlorfenvinphos (considered as priority substances (PS) by the European Commission) TiO_2 photocatalysis (200 mg/L) and photo-Fenton were used. New twin 75-L compound parabolic collector (CPC) pilot plants were used for performing the test which was driven by solar energy. Behaviour was almost similar with single compounds and mixtures of all of them up to more than 100 mg/L. Very low concentration of iron is sufficient to degrade the pesticides. Photo –Fenton treatment appeared to be shorter than TiO_2 degradation **(Maldonado et al., 2007).**

Me´ndez-Arriaga et al., 2010 studied the degradation of ibuprofen (IBP) by photo-Fenton process. Initial concentration of IBP used was 0.87mM and its degradation was directly proportional to amount of H2O2 (.04mMand 0.32mM) used in presence of 1.2 mM of Fe(II). 40 % TOC removal was achieved during mineralization in photo-Fenton where as it was just 10% in case of dark Fenton. It was observed that there is strong binding ability between IBP and iron. The decarboxylation of IBP is promoted by photolability of the Fe(III)– IBP coordinated complex. Decarboxylated and hydroxylated byproducts of IBP are the main byproducts observed during the reaction.

Membrane anodic Fenton treatment (AFT) treatment was used to degrade carbamate insecticides (fenobucarb, dioxacarb, promecarb, carbofuran, carbaryl, bendiocarb). Both single component and multicomponent system were effectively degraded by AFT. Each carbamate competes for hydroxyl radical but AFT kinetic model was obeyed by each of them. Hydroxyl radical initiates the degradation and rate constants for the reaction and they decrease in the following order: dioxacarb carbaryl > fenobucarb > promecarb > bendiocarb > carbofuran. At higher temperature AFT has higher treatment efficiency. AFT not only removes COD efficiently but also increases the biodegradability. GC-MS techniques were used to determine the degradation products .Substituted phenols were the commonly seen degradation products **(Wang and Lemley, 2003).**

CHAPTER 3

OBJECTIVES OF THE STUDY

The main objective of our study is to treat toxic, non biodegradable 2-Chloro-4-nitrophenol.Our study has following objectives:

1. To study the degradation of 2Cl4NP using slurry photocatalysis and the effect of various parameters like effect of photocatalyst, UV intensity, pH, addition of oxidant, A/V ratio on degradation of 2Cl4NP.
2. To study the degradation of compound 2Cl4NP using TiO_2 immobilized cement and clay beads along with their durability studies
3. To study solar photo-Fenton degradation of 2Cl4NP using Foundry Sand as an alternative iron source.

To the best of our knowledge this is the first reported study of use of clay beads as support materials for TiO_2 immobilization.

CHAPTER 4

MATERIALS AND METHODS

This section deals with various materials and methods used in photocatalytic reactions.

4.1 Pharmaceutical compound

Technical grade (97% pure) 2-Chloro-4-nitrophenol (2Cl4NP), $ClC_6H_3(NO_2)OH$ (fig. 7) was obtained from Sigma Aldrich and was used as such without any further purification. 2Cl4NP is mostly used as an ingredient in pesticides, insecticides and also in pharmaceutical industries. It is mainly found as contaminant in waste water. It is very toxic and hard to remove by conventional biological treatment processes. Full scan of compound was taken with the help of UV- Vis spectrophotometer and maximum absorbance was observed at 266 nm.

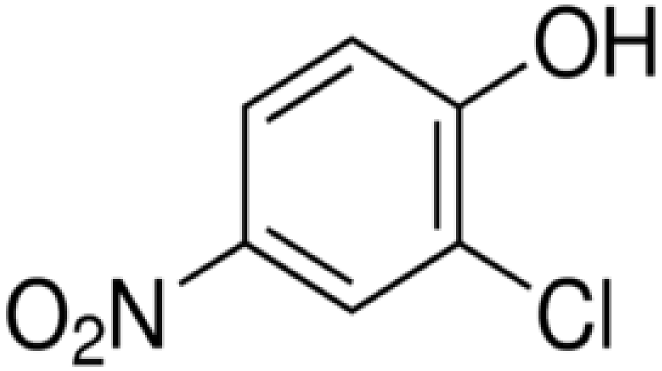

Figure 7: Chemical structure of 2Cl4NP.

4.2 Reagents and Chemicals used

TiO_2 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30) obtained from Evonik Industries, India was used as a photocatalyst. Hydrogen Peroxide, H_2O_2 (Ranbaxy laboratories) was used as an oxidant. pH of the solution was adjusted using 0.1N H_2SO_4. In solar photo-Fenton reaction waste foundry sand (FS) was used which was received from local industry as a gift sample and it was used without any modifications. Double distilled water was used in all the experiments. 50 mgL^{-1} 2Cl4NP solution was used for experimental study. Standard method as per American Public Health Association (APHA) was used to find out Iron **(APHA,**

2012: Sec. 3111(B)), Aluminum (APHA, 2012: Sec. 3111(D)) and COD **(APHA, 2012: Sec. 5220 (D))**.

4.3 Instruments used

4.3.1 pH meter

The pH of the solution was monitored by pH meter and pH of the solution was adjusted using 0.1N H_2SO_4. Freshly prepared buffer solutions (pH 4 and 9) were used to calibrate the instrument weekly.

4.3.2 Magnetic stirrer

Magnetic stirrer was used in experiments for proper mixing of the catalyst in the solution and to make solution remain in suspension.

4.3.3 Aerators

To oxidize the organic matter air is continuously supplied with air spargers.

4.3.4 Filters

Filters of pore size 0.45 µm (Millipore) were used to filter the samples obtained from photocatalytic reaction.

4.3.5 UV-Visible Spectrophotometer

The spectrum for analysis of 2Cl4NP was taken with UV-Vis Spectrophotometer (Hitachi V- 500 UV/VIS (Japan) double- beam spectrophotometer) at 266nm.

4.3.6 Muffle Furnace

To fix catalyst coating on clay beads and cement beads muffle furnace (temperature range 200 to 1200 ^{0}C) was used. It was operated at a temperature of 200 °C for this purpose.

4.3.7 Branson bath sonicator

Sonicator (model no. EN 60 US) having 33 KHz frequency was used for homogenization of catalyst suspension which was used for coating of clay and cement beads.

4.3.8 COD Digester

COD Digester (Hach, DRB 200) was used for digestion of samples in COD determination.

4.4 HPLC Analysis

HPLC [Shimazdu, SED-20A] analysis was carried out for confirming 2Cl4NP degradation. HPLC was conducted through binary HPLC system with C-18 column (250 mm × 4.60 mm), particle size 5 µm using acetonitirile:water (70:30) as mobile phase with UV detector at 266 nm for 2Cl4NP. Flow rate was maintained at 1.0 mL min^{-1}. Injection volume was 20 µl and each analysis lasted 4.309 min.

4.5 SEM-EDS Analysis

SEM (JSM-6510LV, JEOL, Japan) and EDS (INCAX-act, Oxford instruments, United Kingdom) were used to analyze the clay and cement beads.

4.6 UV reaction chamber details and reactor used

Borosil glass bowls, 17cm in diameter and 5 cm in height having capacity of 1000ml were used as batch rector for photocatalytic reactions. This glass reactor was placed on lab jack in UV wooden chamber having dimensions of 1.37 m× 0.9 m ×1.0 m. 36W UV tubes (Philips) were attached on the underside of the roof of chamber which have wavelength of 365nm to get required density for degradation **(Toor et al., 2006**). The UV intensity was varied between 10 to 24 Wm^{-2}, by adjusting the distance between reactor and the tubes. For controlling the temperature of chamber an exhaust fan was provided.

4.7 Methodology for Heterogeneous photocatalysis using TiO_2 in slurry form

4.7.1 Preparation of stock solution

The stock solution was prepared by adding known amount of compound in double distill water in 1-liter volumetric flask and it was filled upto the mark with double distill water and was kept for stirring for overnight. In our case stock solution of $50mgL^{-1}$ was made with double distill water by dissolving 50mg of 2Cl4NP in 1L of double distill water and the solution was stored at room temperature.

4.7.2 Experimental Procedure

1. $50mgL^{-1}$ solution of 2Cl4NP was prepared by double distill water for photocatalytic reaction.
2. 200 mL of this solution was taken in shallow pond slurry reactor, known amount of catalyst TiO_2 and oxidant H_2O_2 were added.
3. This was kept on magnetic stirrer for continuous stirring and oxygen was supplied through aerators under UV irradiations in wooden chamber (fig. 8).
4. At regular intervals of time sample was collected (3-4 ml) from the vessel and was filtered through 0.45µm Millipore syringe filter.
5. Analysis of these samples was done by UV-Vis Spectrophotometer at 266nm.

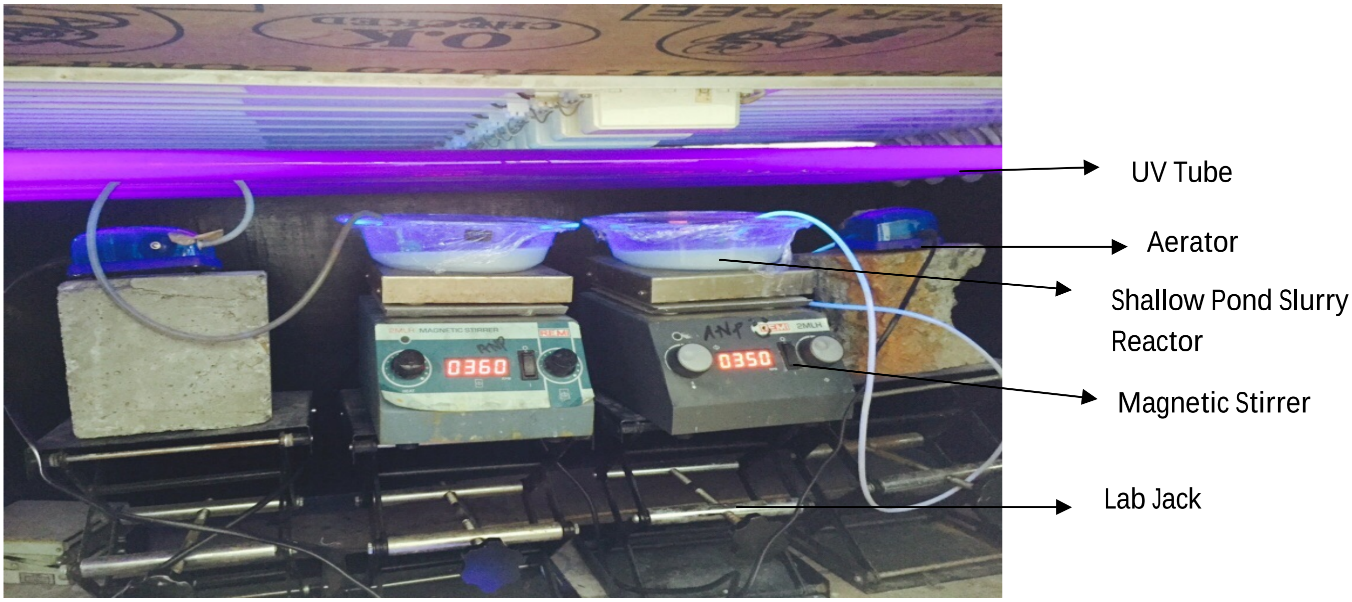

Figure 8: Lab Scale Slurry Reactor in UV Light.

Process optimization was done by varying parameters like effect of catalyst (TiO_2) concentration, pH, effect of H_2O_2, UV intensity, A/V ratio of the reactor.

4.8 TiO_2 Immobilization on cement and clay beads

Different sized spherical cement beads (around 200 in number) were made manually using appropriate amount of cement and sand. Around 50 beads of uniform size were chosen for immobilization. Similarly spherical shaped clay beads were made using clay. Beads were coated with TiO_2 as mentioned in previous studies **(Verma et al., 2014).**Similar method was followed to coat clay beads. Fig 9(a) and 9(b) shows TiO_2 coated cement and clay beads respectively.

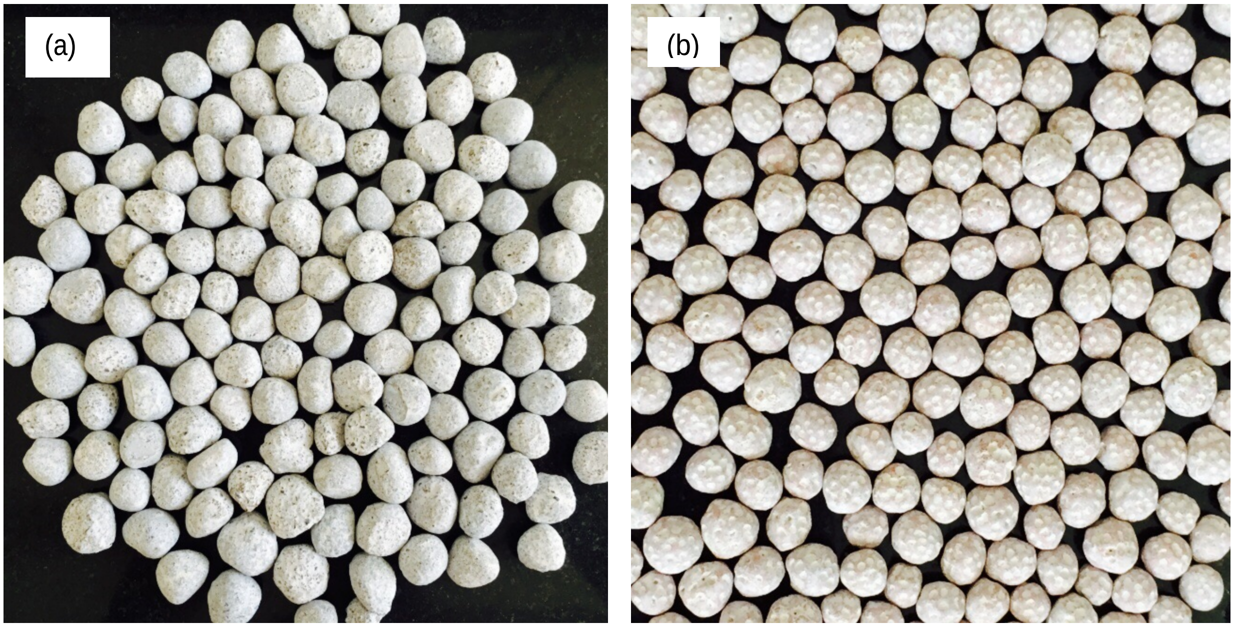

Figure 9: (a) TiO_2 coated cement beads and (b) TiO_2 coated clay beads.

4.8.1 Experimental Procedure

1. Same shallow pond reactors were used to perform fixed bed photocatalysis.
2. 200 ml of 2Cl4NP solution was used and required numbers of cement and clay beads were used so as to cover the bottom surface of the reactor.
3. The reaction was performed in both UV and sunlight. Two spargers were provided at a time for aeration (fig. 10).

4. After regular intervals sample was collected and analyzed using UV-Vis Spectrophotometer at 266 nm.

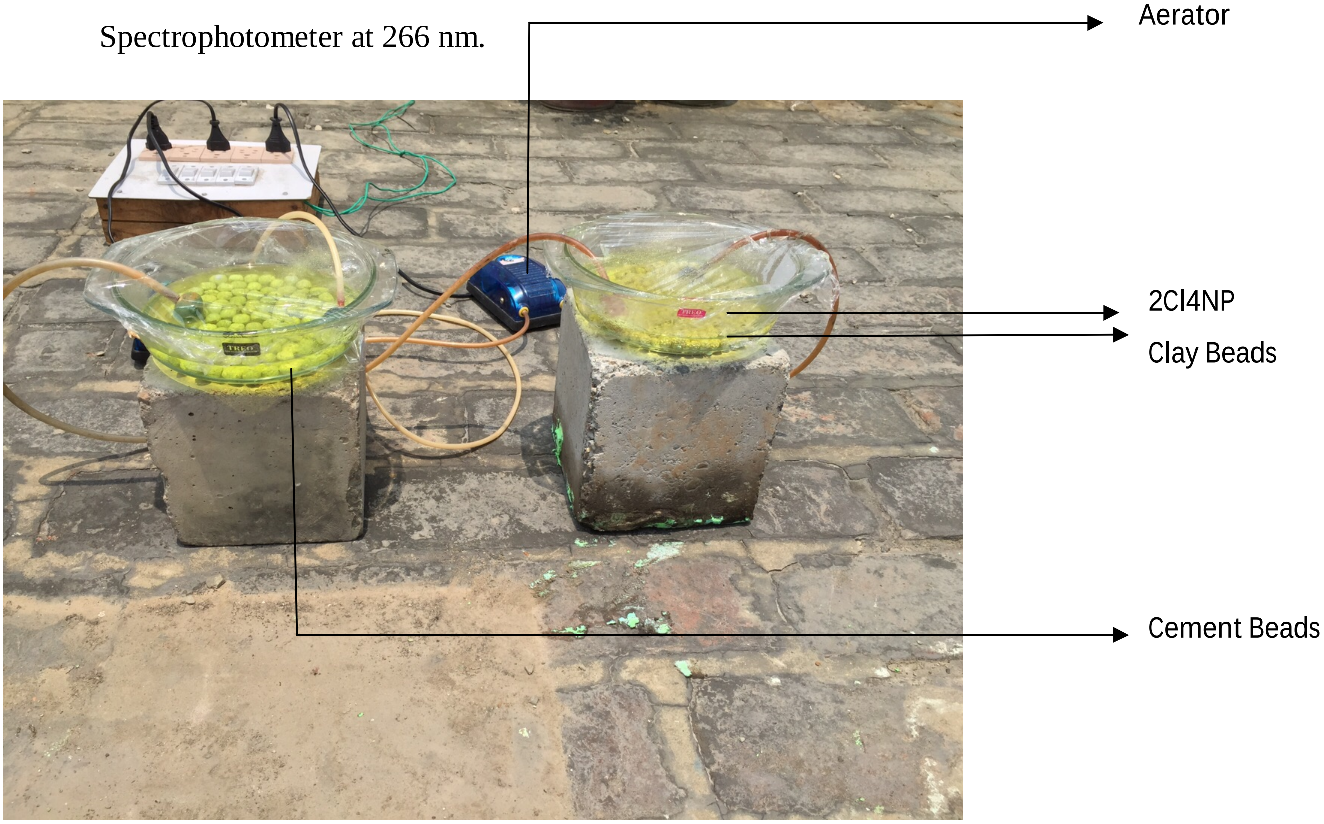

Figure 10: Lab Scale Slurry Reactor (TiO_2 immobilized on cement and clay beads) in Sunlight.

4.9 Methodology for Heterogeneous photocatalysis by solar photo-Fenton

Experimental Procedure

1. 50mgL^{-1} solution of 2Cl4NP was prepared by double distill water for photocatalytic reaction.
2. 200 mL of this solution was taken in shallow pond slurry reactor, known amount of FS and oxidant H_2O_2 were added.
3. For continuous stirring solution was kept on magnetic stirrer and aerators were used to provide oxygen during the reaction.
4. Set up was placed in sunlight (fig. 11).

5. Sample was collected at regular intervals of time and 0.45 µm syringe filter was used to filter the sample. Spectrophotometric analysis of the sample was done at 266nm.

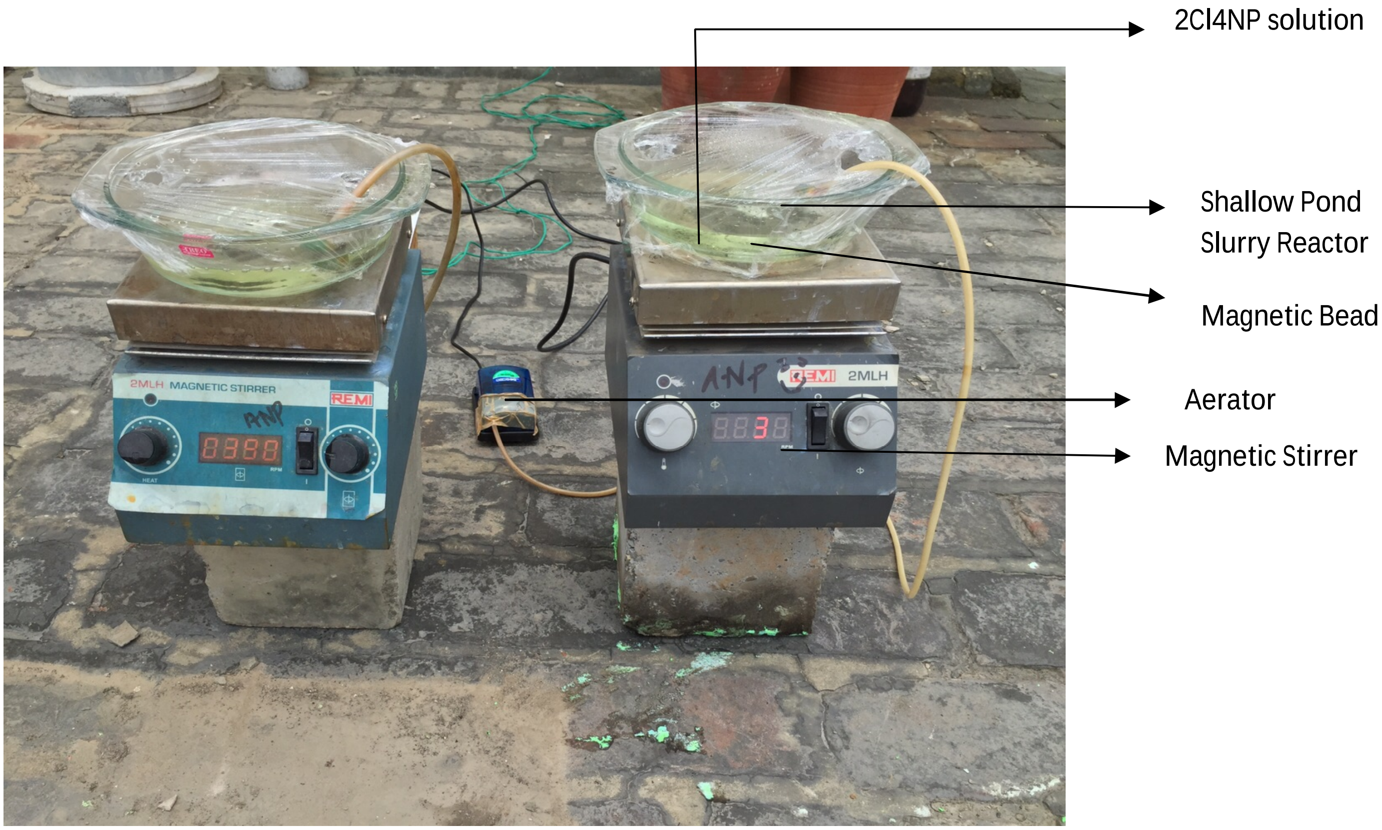

Figure 11: Shallow Pond Slurry Reactor in sunlight (heterogeneous solar photo-Fenton process).

Process optimization was done by varying parameters like effect of H_2O_2, effect of FS concentration. All experiments were performed thrice for reproducibility of results. For all the experiments the standard deviation was in the range of 3-5%.

CHAPTER 5

RESULTS AND DISCUSSION

This sections deals with detailed studies of photocatalytic degradation of 2Cl4NP using slurry, immobilized photocatalytic process and heterogeneous solar photo-Fenton process. Various parameters like effect of catalyst (TiO_2) concentration, pH, effect of H_2O_2, UV intensity, A/V ratio of the reactor, FS concentration were studied and optimized.

5.1 Calibration Curve of 2Cl4NP

Full scan of the 2Cl4NP was taken and λ_{max} was found 266 nm. Accordingly standard calibration curve (fig. 12) of 2Cl4NP was made using known different concentrations (10-80mgL^{-1}) at 266nm. Value of slope is 0.022 and R^2 is 0.996l. From this curve, the unknown concentration of solution can be calculated and kinetics of the degradation can be studied.

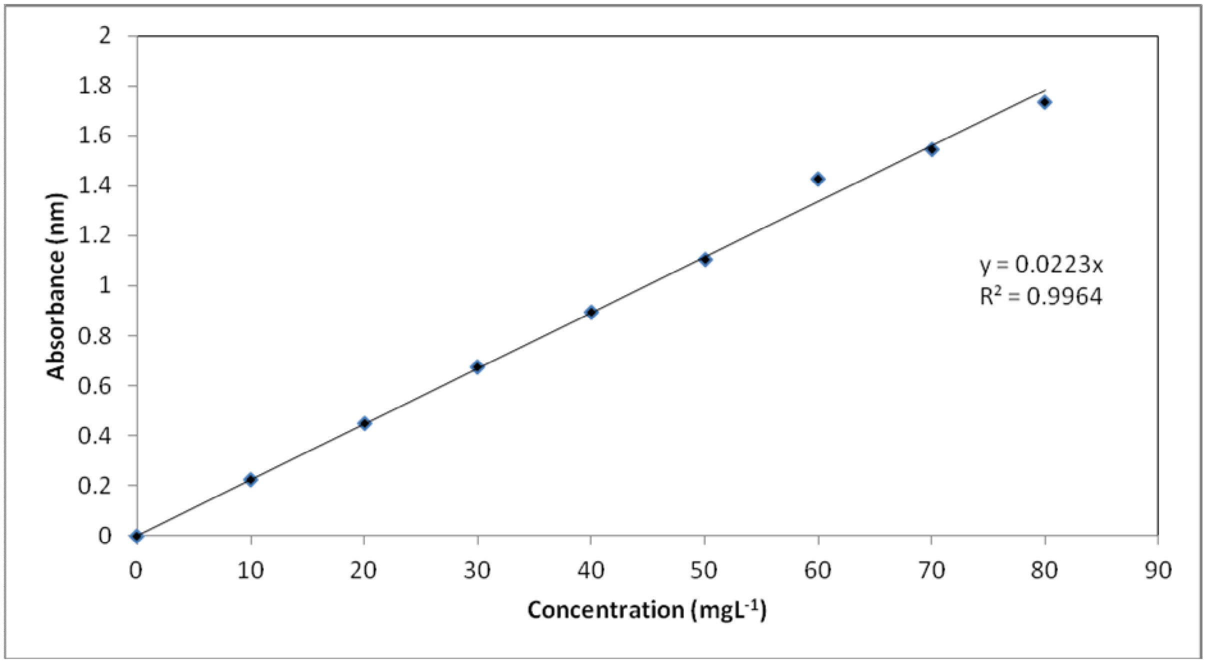

Figure 12: Standard calibration curve of 2-Chloro-4-nitrophenol.

5.2 Degradation Studies Using Heterogeneous (slurry) TiO_2 photocatalysis:

5.2.1 Preliminary Studies

In the current study, adsorption and photolytic experiments were carried out as control prior to photocatalytic studies. Photolysis studies were performed in a batch reactor by irradiating the 2Cl4NP solution in UV light (UV only) in the absence of photocatalyst in which only negligible amount of degradation (6%) was observed. Adsorption studies (TiO_2 only) showed 7.5% reduction in the concentration of 2Cl4NP which may be due to the development of monolayer of pollutant on the surface of catalyst. The formation of monolayer blocks all active sites on the surface of catalyst due to which no further decrease in degradation was observed. While in the presence of oxidant (H_2O_2 only) almost 10% degradation of the compound was observed. Combination of H_2O_2 + TiO_2 + UV showed best degradation (91.75%) in 120 min. It can therefore be presumed that adsorption-desorption of 2Cl4NP along with reaction intermediates are reasonably slower than electron/hole pair formation **(Verma et al., 2014).**

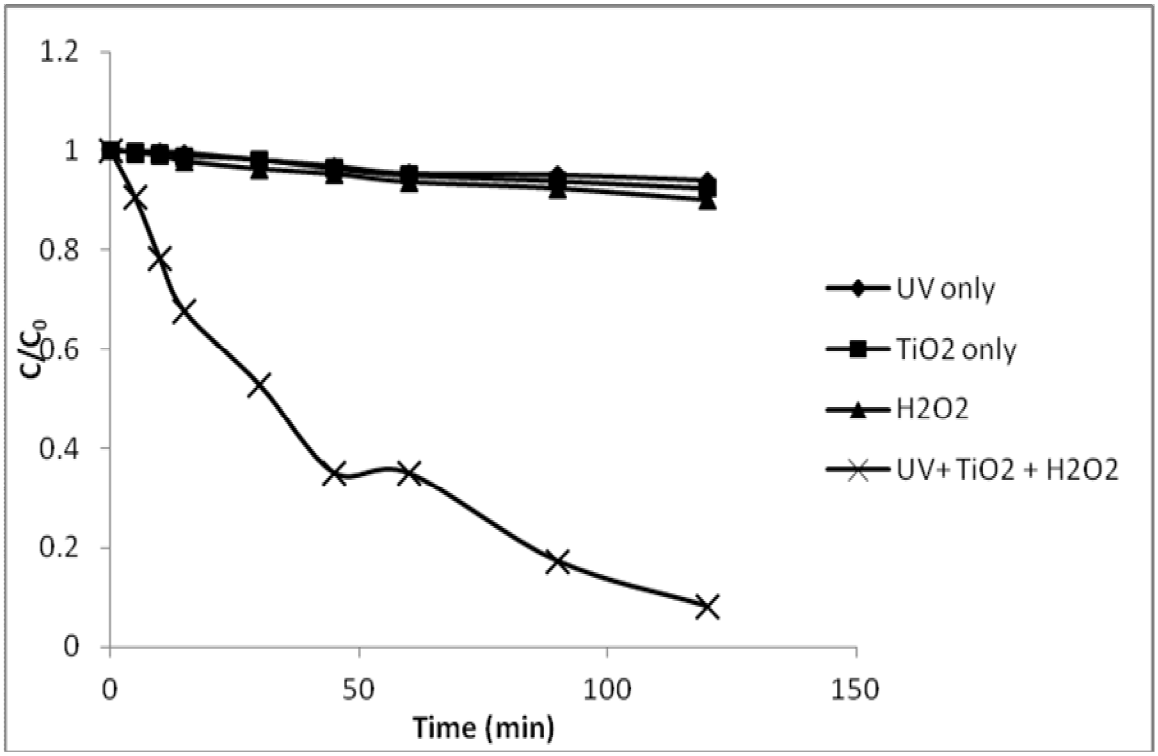

Figure 13: Preliminary experiments perfomed under different conditions to evaluate their effciency towards degradtion of 2Cl4NP.

5.2.2 Effect of TiO_2 concentration

Photocatalyst concentration greatly affects the rate of photocatalytic reaction, so it is necessary to optimize the catalyst concentration in solution. Also catalyst concentration should be optimized to ensure total absorption of efficient photons and to avoid excess catalyst **(Saquib and Muneer, 2003)** because light penetration in solution is reduced and unfavourable light scattering occurs **(Chun et al., 2000).** TiO_2 was used as a catalyst and its concentration was varied between 0.025-1.5 gL^{-1}. The effect of catalyst concentrations on the degradation of 50 mg/L 2Cl4NP in the batch glass reactor is shown in fig. 14. Studies show that initially degradation rate increases with increase in the catalyst loading from 0.025-0.75gL^{-1} and then either becomes constant or decreases because of light scattering effect. Even though, with increase in catalyst concentration, number of active sites increase but after certain concentration light penetration is compromised because of excessive particle concentration. At high catalyst concentration, the tendency to agglomerate increases, which results in decrease in catalyst surface area available for light absorption and degradation rate decreases. The optimized dose of photocatalyst selected in our study was 0.75 gL^{-1}.

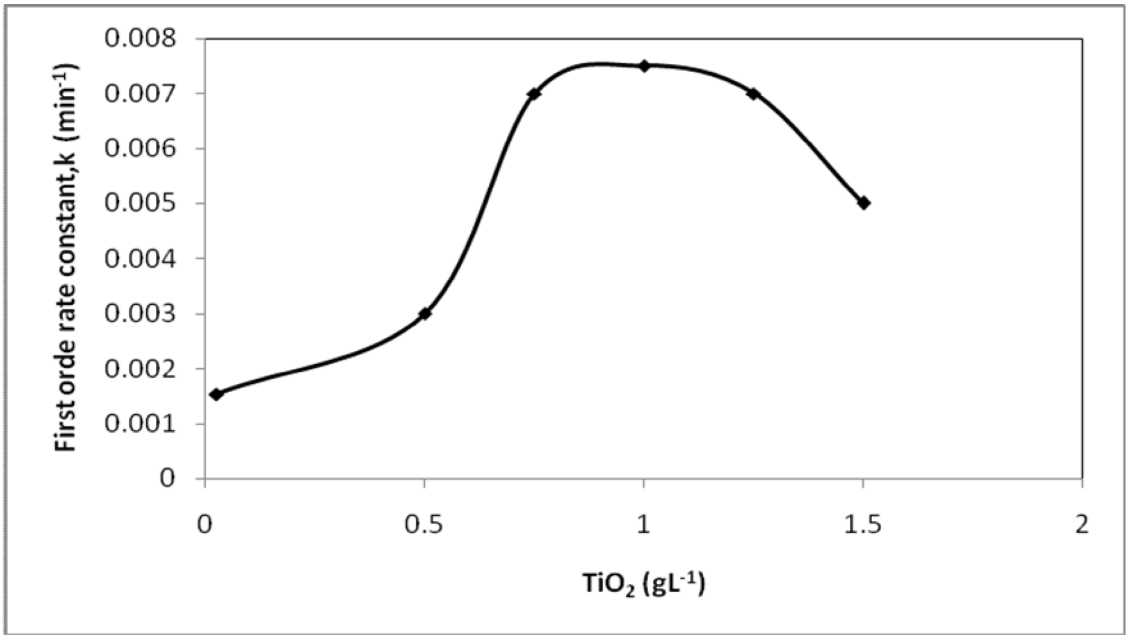

Figure 14: Plot of variation in TiO_2 vs first order rate constant, k during photocatalytic degradation of 2Cl4NP (C_0=50 mgL^{-1}, V=200 mL).

5.2.3 Effect of pH

pH of the solution is an important factor affecting the photocatalytic reactions occurring on the particle surfaces as the surface charge properties of the catalyst and size of aggregates it forms is affected by it **(Haque and Muneer, 2007).** In the present study pH was varied between 4 and 9 with optimized dose of TiO_2 i.e. 0.75 gL^{-1}. According to present study, maximum degradation was achieved in acidic conditions at pH 4 (fig. 15). The value of degradation rate constant k decreased from 0.008976 min^{-1} to 0.001 min^{-1} with increase in the pH from 4 to 9. As a result, pH 4 was optimized to carry out further studies.

According to **Okamoto et al., 1985** the mechanism for photocatalytic reaction in the presence of titanium dioxide is shown in following reactions (13-20).

$$TiO_2 \longrightarrow h^+ + e^- \qquad (13)$$

$$H_2O + h^+ \longrightarrow {}^{\cdot}OH + H^+ \qquad (14)$$

$$OH^-_{(s)} + h^+ \longrightarrow {}^{\cdot}OH \qquad (15)$$

$$O_2 + e^- \longrightarrow {}^{\cdot}O_2^- \qquad (16)$$

$${}^{\cdot}O_2^- + H^+ \longrightarrow {}^{\cdot}HO_2 \qquad pKa = 4.88 \quad (17)$$

$${}^{\cdot}HO_2 + {}^{\cdot}HO_2 \longrightarrow H_2O_2 + O_2 \qquad (18)$$

$$H_2O_2 + O^- \longrightarrow {}^{\cdot}OH + OH^- + O_2 \qquad (19)$$

$$H_2O_2 \longrightarrow 2\,{}^{\cdot}OH \qquad (20)$$

When pH value is higher than pKa (4.88) for HO_2 radical, the reaction proceeds in the reverse direction. The lack of HO_2 radicals make reactions difficult to proceed. Therefore, the formation of OH free radicals was supplied by the reaction of positive holes with water and OH^- on the surface of titanium dioxide. **Okamoto et al., 1985,** also found that the formation of OH free radicals being mainly from H_2O_2, which would not favor the decomposition of 2Cl4NP at a high pH region.

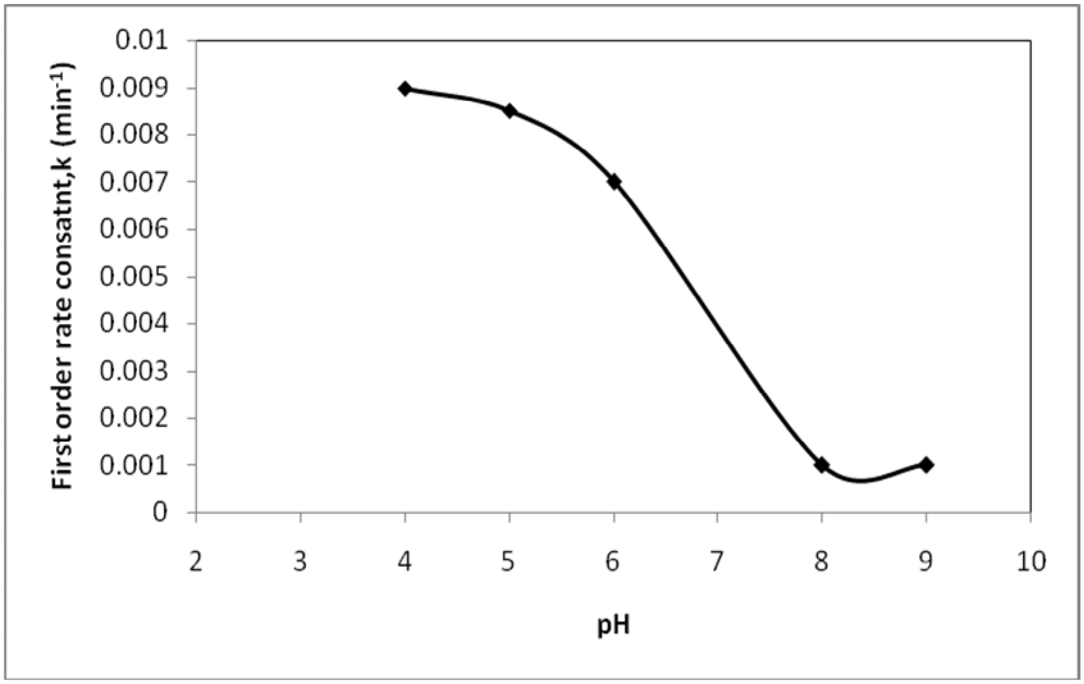

Figure 15: Plot of variation in pH vs first order rate constant, k during photocatalytic degradation of 2Cl4NP (C_0=50 mgL^{-1}, V=200 mL).

5.2.4 Effect of oxidant (H_2O_2) addition

The recombination of electron/hole is one of the major implications that usually occur in case of TiO_2 photocatalysis. The addition of oxidant or electron acceptor generally prevents this recombination step and thus quantum yield is not affected. In our study, H_2O_2 was used as an electron acceptor and was varied from 0.05 to 0.3 mL/200mL to determine the optimum concentration. The oxidant addition not only prevented the recombination of electron/hole by acquiring the electron from the conduction band but also promoted production of more oxidizing species and hydroxyl radicals thereby improving the degradation rate **(Singh et al., 2007a, 2007b)**. Fig. 16 shows that rate constant of degradation reaction of 2Cl4NP initially increased from 0.013 min^{-1} to 0.017 min^{-1} when H_2O_2 was added in the range 0.05-0.1 mL/200mL. Thereafter, degradation rate started declining as scavenging effect of electron/hole predominates at higher concentration of H_2O_2 and formation of HO_2 occurs **(Zhao et al., 2004)**. Maximum degradation (97.19 %) of the compound was achieved with 0.1 mL/200mL of H_2O_2 at optimized dose of TiO_2 (0.75 gL^{-1}), pH 4 after 210 min of photocatalytic treatment.

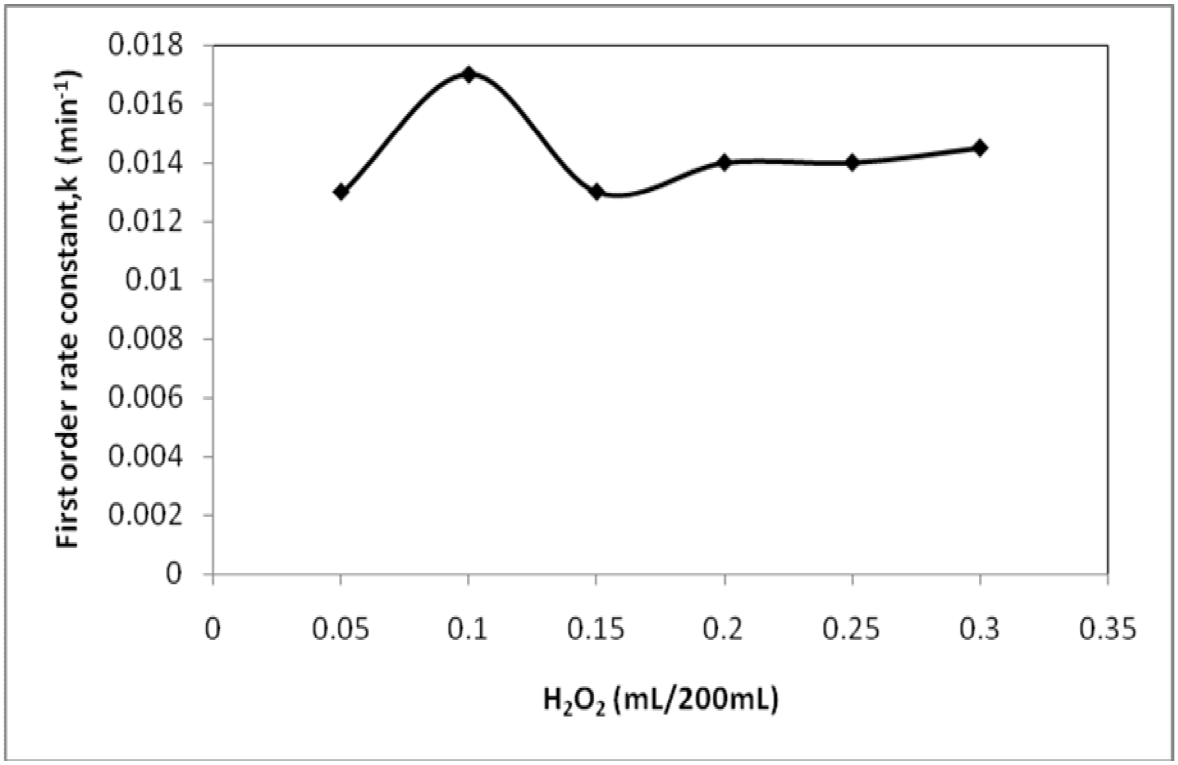

Figure 16: Plot of variation in H_2O_2 vs first order rate constant, k during photocatalytic degradation of 2Cl4NP (C_0=50 mgL^{-1}, V=200 mL, pH=4).

5.2.5 Effect of UV intensity

Radiation absorption capacity of catalyst greatly affects the photocatalyst reaction rate **(Curco´ et al., 2002).** According to **Qamar et al., 2006; Karunakaran and Senthilvelan, 2005,** with increase in light intensity degradation rate also increases. Reaction pathway is not affected by nature or form of light **(Stylidi et al., 2004).** In the present study, UV intensity was varied between 10 to 25 Wm^{-2} keeping area by volume constant and optimized conditions of 50 mgL^{-1} of 2Cl4NP solution, 0.75gL^{-1} TiO_2 and 0.1 ml H_2O_2, pH=4. The rate constant increased from 0.014 to 0.017 min^{-1} for 10 to 25 Wm^{-2} UV intensity. This might be because of increase in the production of electron hole pair on the surface of photocatalyst with increase in light intensity thereby improving the oxidation of organic pollutant. Further studies were carried out at maximum UV intensity i.e. 25 Wm^{-2} which showed better degradation of 2Cl4NP.

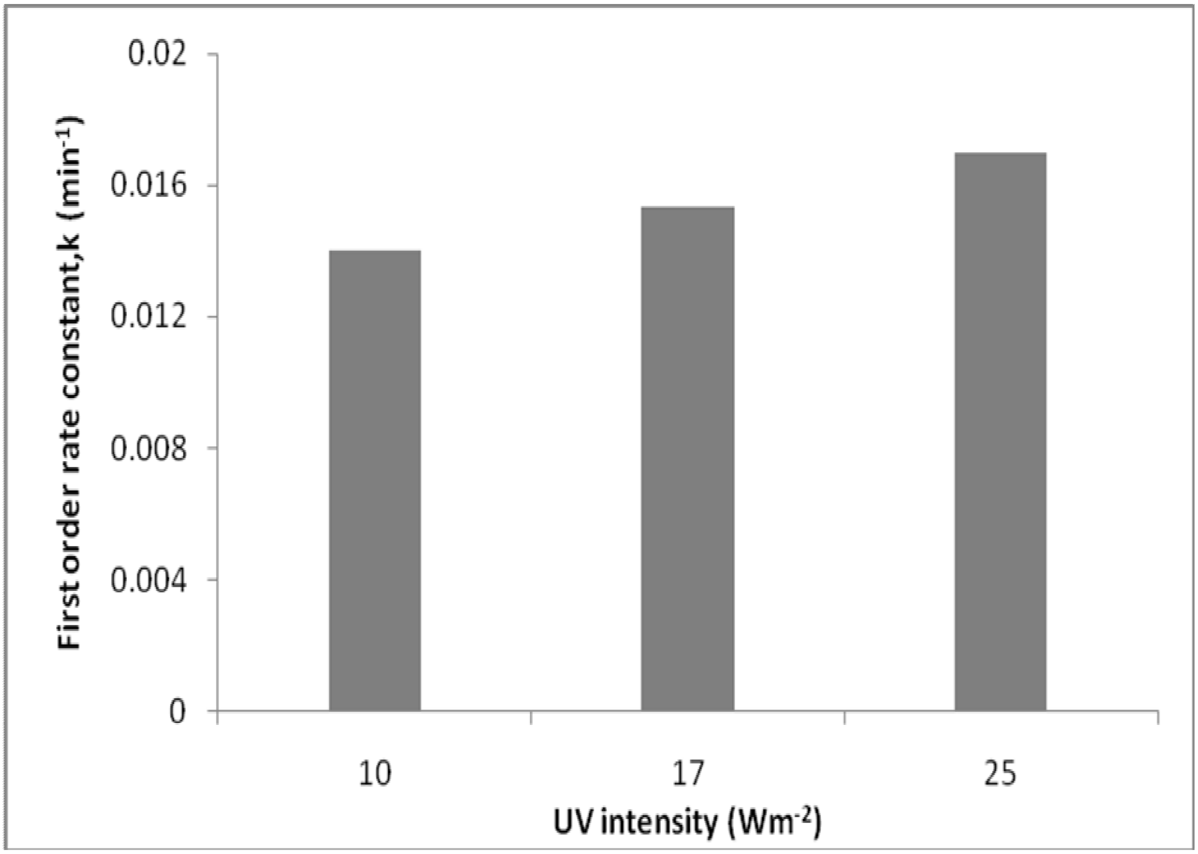

Figure 17: Plot of variation in UV intensity vs first order rate constant, k during photocatalytic degradation of 2Cl4NP (C_0=50 mgL^{-1}, V=200 mL, pH=4).

5.2.6 Effect of A/V ratio of the reactor

The depth of solution in the reactor is very important in photocatalytic degradation reactions. For effective penetration of light (either UV or solar) more area and less depth is required **(Toor et al., 2006).** Area by Volume (A/V) of the reactor was varied between 0.90746-2.26865 cm^{2}mL^{-1}. In our case, A/V was varied by varying the volume of solution used in the reactor keeping the exposed area constant. A/V can also be varied by keeping volume of the solution constant and varying the area of exposure. As the volume of the solution decreased its degradation rate constant increased from 0.011 min^{-1} to 0.02 min^{-1} as shown in fig. 18. Increase in degradation is because depth of the solution decreases due to which path length of photons entering the solution increases, resulting in elevated OH radicals **(Verma et al., 2014).**

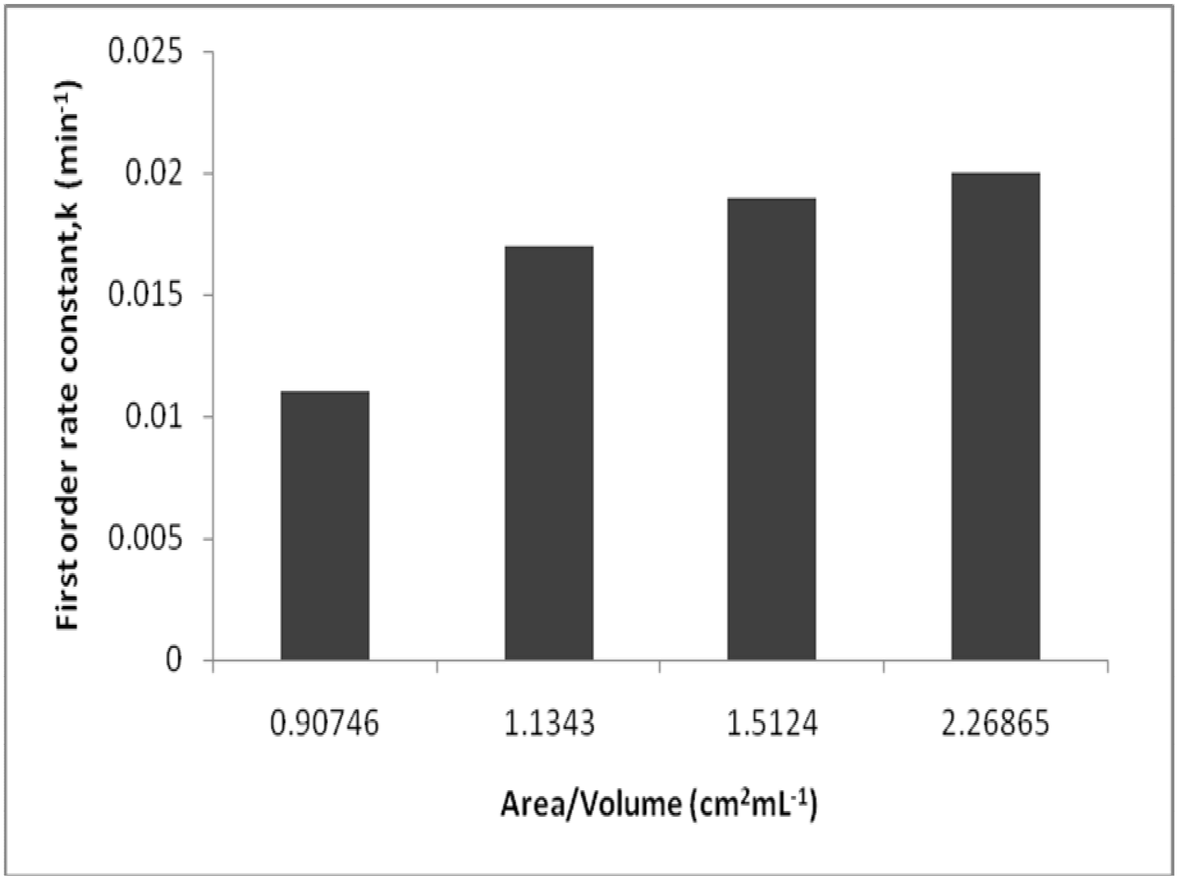

Figure 18: Plot of variation in A/V ratio vs First order rate constant, k during photocatalytic degradation of 2Cl4NP (C_0=50 mgL^{-1}, V=200 mL, pH=4, TiO_2= 0.75 gL^{-1}).

5.2.7 Comparison of UV and solar radiations

Advanced oxidation process leads to the formation of non selective and highly reactive hydroxyl radical but the major disadvantage associated with it is the high cost of UV-lamps and electricity **(Rosenfeldt et al., 2006).** By using sunlight, the above drawback can be overcomed. As sunlight is lavishly available it can be utilized for carrying out the degradation of organic pollutants. In our study experiments were conducted in both UV and natural solar light at optimized conditions i.e. pH 4, 200 mL solution, 0.75 gL^{-1} TiO_2 and 0.1 mL H_2O_2. Degradation was better in solar light (95.83%) as compared to UV light (91.7 %) after 2 hrs of treatment as shown in fig. 19. **Priya et al., 2008** carried out similar kind of study proving solar treatment is better for degrading as compared to artificial UV light.

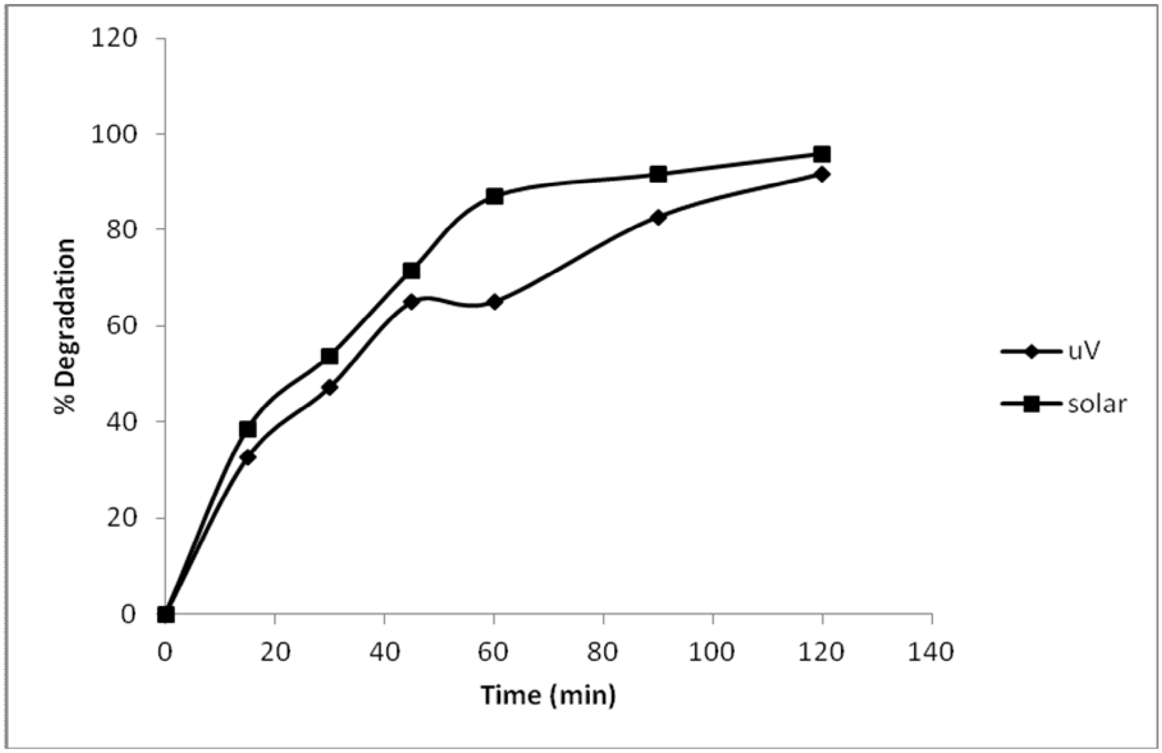

Figure 19: Comparison between Artificial UV light and solar light at optimum conditions (C_0=50 mgL^{-1}, V=200 mL, pH=4, TiO_2= 0.75 gL^{-1}, H_2O_2=0.1 mL/200mL).

5.3 Degradation Studies using fixed bed photocatalysis

5.3.1 Degradation of 2Cl4NP using Immobilized TiO_2 on cement and clay beads:

Degradation of 2Cl4NP is better with TiO_2 in slurry form as it is in direct contact with UV radiation in photoreactor. But from economical and practical point of view it has some disadvantage that catalyst needs to be removed after the treatment. As a result efforts have been done to study immobilized systems with different routes and different support system **(Byrne et al., 1998; Rachel et al., 2002; Aguado et al., 2006).** In comparison with powder TiO_2, immobilized TiO_2 have lower photocatalytic activity because restrictions for mass transfer increases and interfacial area available decreases but the need of catalyst removal after the treatment is eliminated. Also long stability of TiO_2 is guaranteed, which avoids the leaching of TiO_2 particles in the solution and catalyst can be regenerated in case of deactivation **(Parra et al., 2004).** Experiments were conducted in sunlight using appropriate number of cement beads and clay beads in a batch reactor containing aqueous solution of the 2Cl4NP at all conditions optimized in slurry photocatalysis. 68% and 52% degradation of 2Cl4NP was obtained after 5 h of photocatalytic treatment using cement beads and clay beads respectively. Actually the pH of the solution continuously increased during the course of reaction due to which degradation decreased (as discussed in section 5.2.3). For this reason, the acidic pH of the solution was maintained by continuous addition of acid to sustain the degradation of 2Cl4NP. With certain modifications, a continuous/semi-continuous solar reactor can be designed with optimized parameters for field-scale applications. In fact this is first reported study for the degradation of 2Cl4NP using clay beads and cement beads as inert support material for immobilization of catalyst.

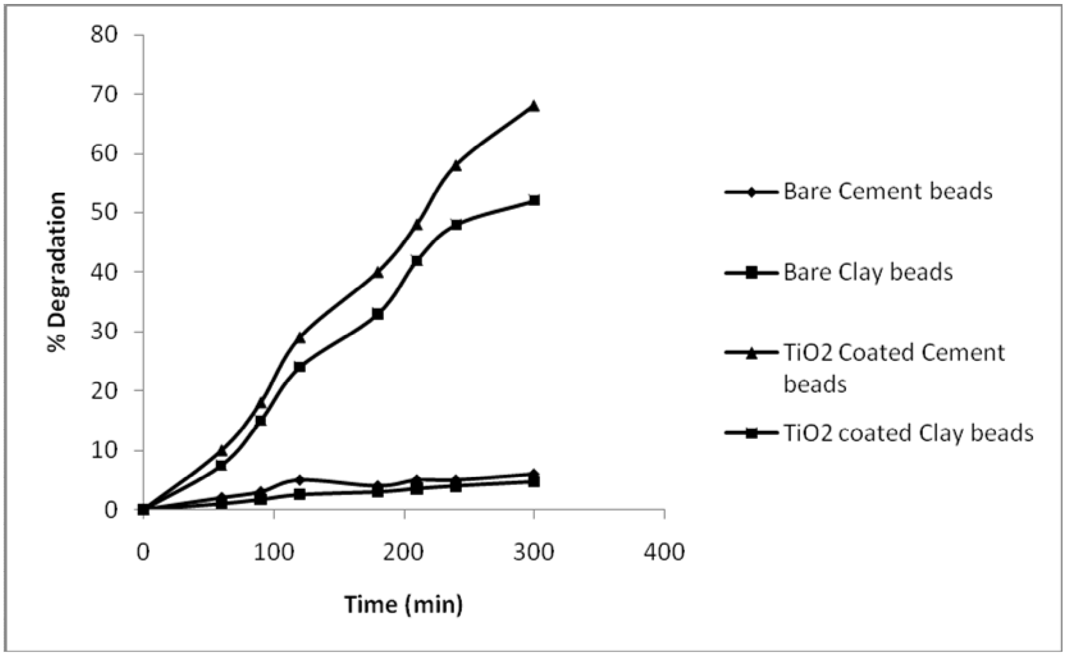

Figure 20: Degradation of 2Cl4NP by bare cement and clay beads and effect of TiO_2 coated cement and clay beads (C_0=50 mgL^{-1}, V=200 mL, TiO_2= 0.75 gL^{-1}, H_2O_2=0.1 mL/200mL).

5.3.2 Recyclability Studies:

In fixed-bed photocatalysis durability of the supported catalyst is very important. The photocatalytic activity of immobilized catalyst decreases after certain runs due to either catalyst fouling or loss of catalyst from the surface. Some studies have reported high temperature (480°C) reactivation of the catalyst, which is generally not good from economical point of view. In this view, efforts have been done to check the durability of immobilized catalyst on cement and clay beads for the degradation of 2Cl4NP. The cement and clay beads were recycled for 10 cycles without much decrease in its photocatalytic efficiency for degradation of 2Cl4NP as shown in fig. 21(a). For reactivation of the beads, they were heated in oven or muffled at 100°C for one hour after every cycle. Photocatalytic activity of the beads may have reduced somewhat because of the loss of catalyst during the reaction or blocking of catalyst sites. Scanning electron microscope (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) analysis showed that catalyst was intact on clay and cement beads even after 10 cycles as shown in fig. 21(b) and 21(c), which proved its stability. More effective methods of catalyst immobilization, durable support and efficient reactor design can prevent/minimize the aforesaid problems.

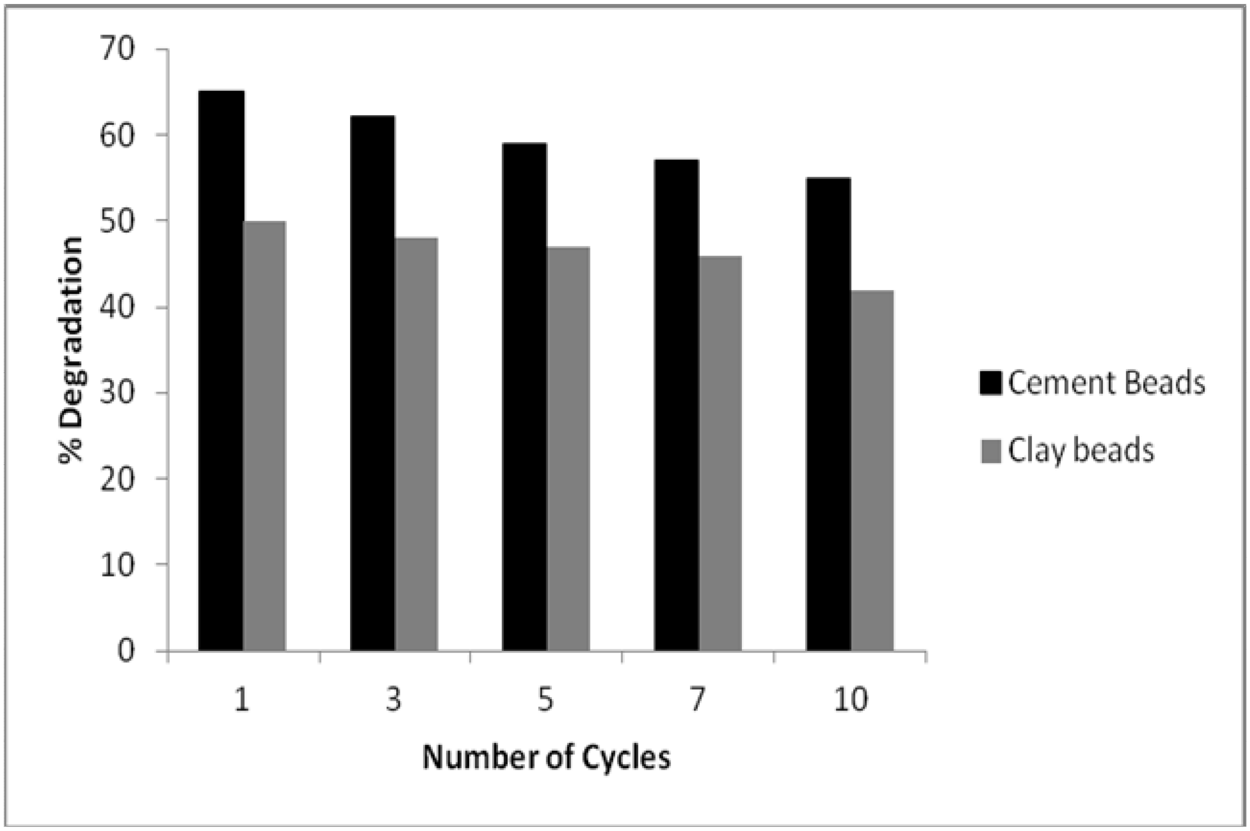

Figure 21 (a): Recyclability Studies of TiO_2 coated cement and clay beads for the degradation of 2Cl4NP (C_0=50 mgL^{-1}, V=200 mL, TiO_2= 0.75 gL^{-1}, H_2O_2=0.1 mL/200mL).

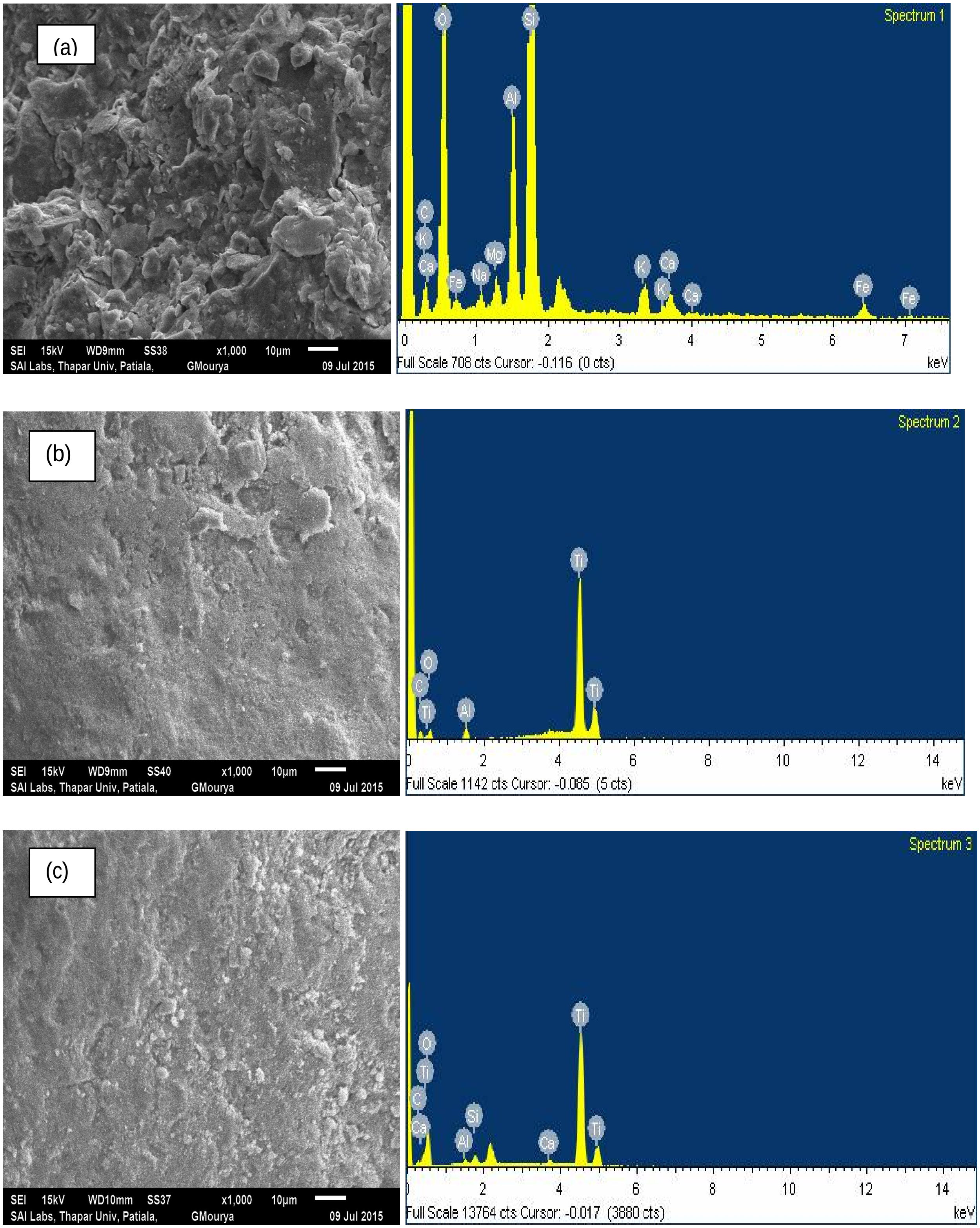

Figure 21 (b): SEM images (a) blank clay bead without TiO_2 coating (b) freshly coated TiO_2 clay bead (c) used clay bead after 10 cycles along with their EDS data.

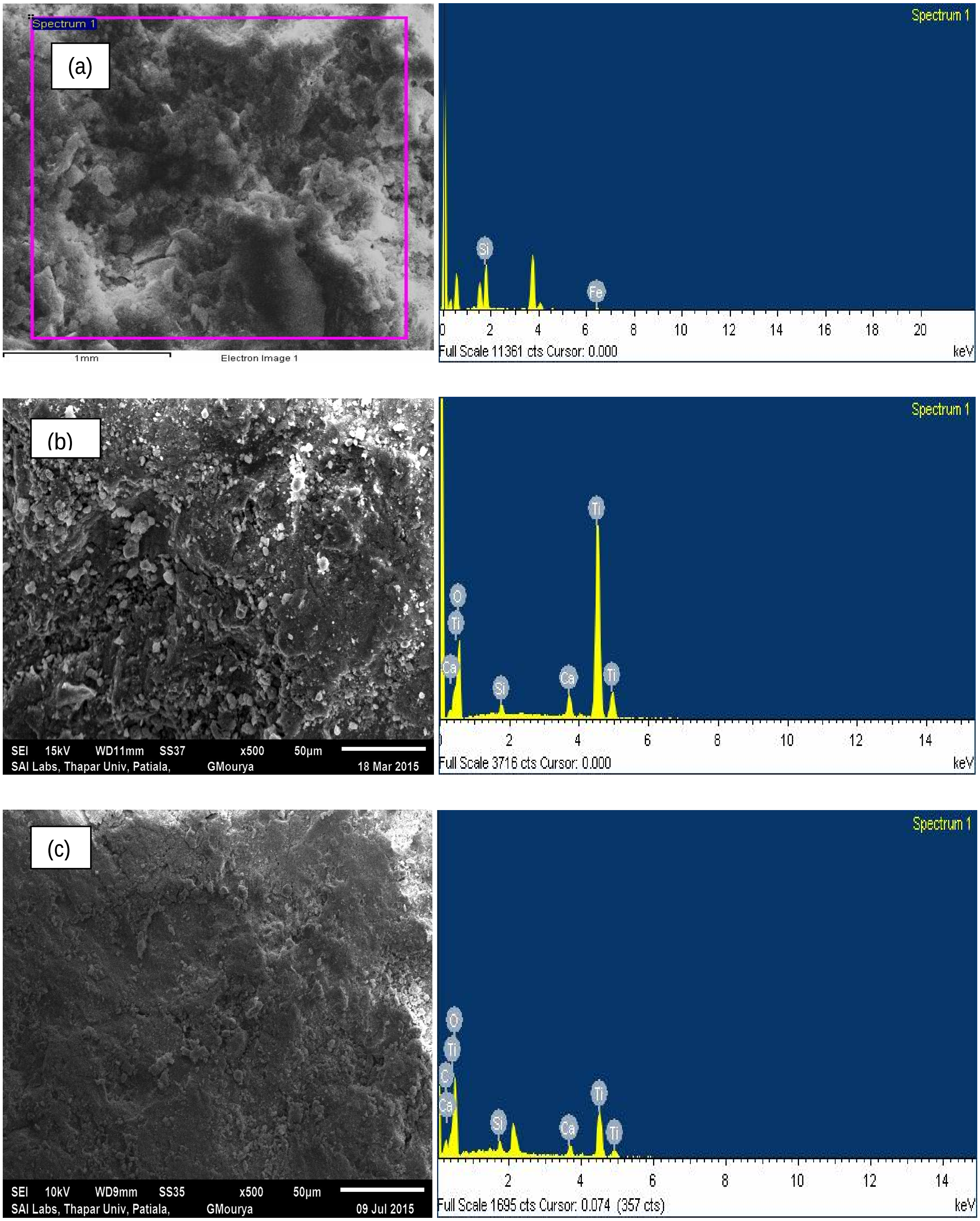

Figure 21(c): SEM images (a) blank cement bead without TiO_2 coating (b) freshly coated TiO_2 cement bead (c) used cement bead after 10 cycles along with their EDS data.

5.4 Degradation studies using solar photo-Fenton process

5.4.1 Characterization of Foundry sand (FS):

Foundry sand is used as an alternative iron source in heterogeneous solar photo-Fenton reactions. For the characterization of FS, SEM and EDS was performed. The chemical composition of FS is shown in fig. 22 and Table 3. The results showed that reasonable amount of Iron (23.16%) is present which proves FS's worth as an alternative catalyst. Also absence of heavy metals as indicated by results eliminates their risk of leaching **(Rajput, 2014).**

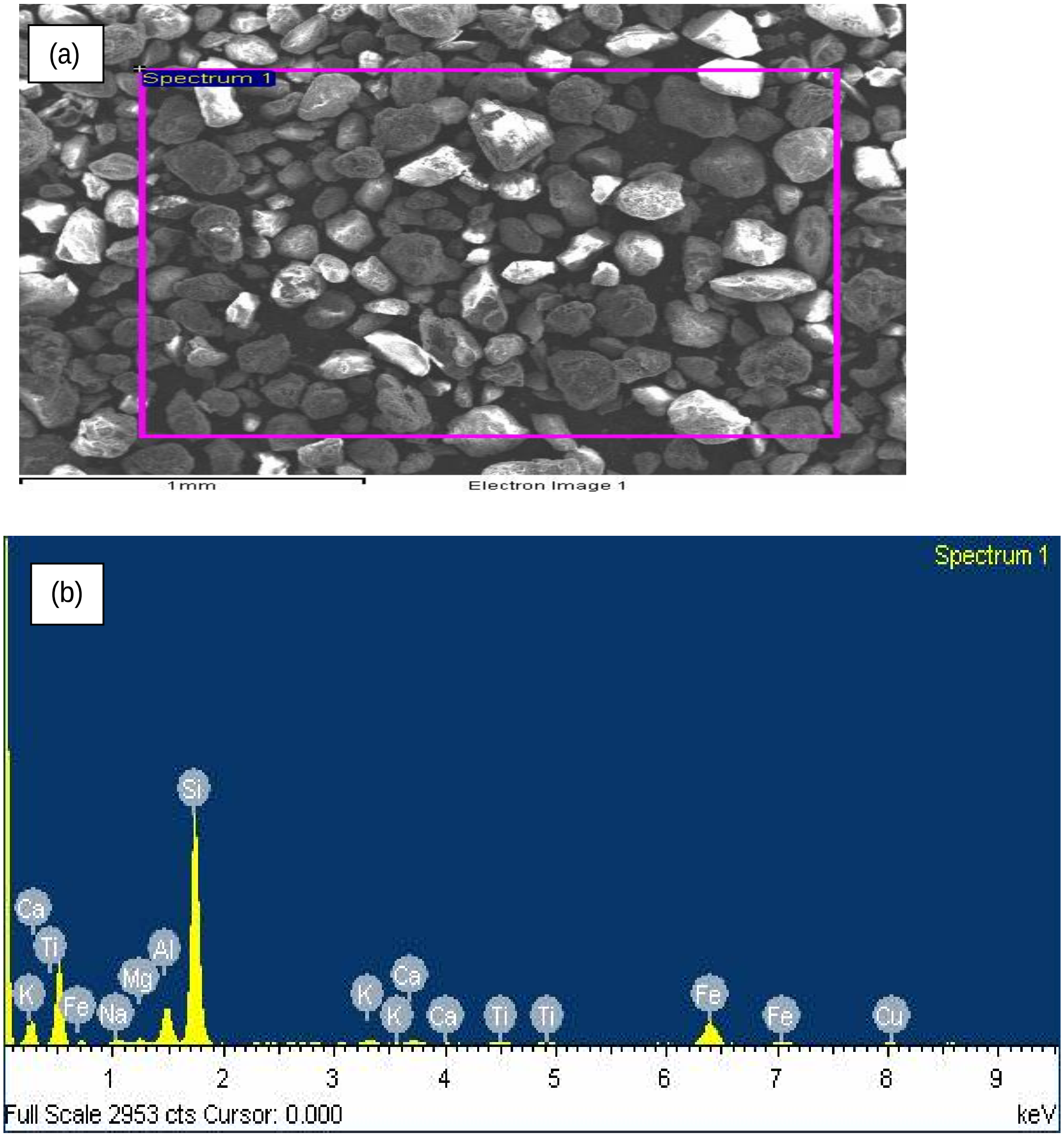

Figure 22: (a) SEM micrograph of FS (b)EDS pattern of FS.

Table 3: 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**
Total	**100.00**	

5.4.2 Effect of H_2O_2

The concentration of oxidant in solution plays a crucial role that relies on the rate of its production and consumption. In order to determine the effect of H_2O_2 concentration on the degradation of 2Cl4NP, it is necessary to optimize the dose of H_2O_2. Fenton reaction is inhibited by excessive amount of hydrogen peroxide as it reacts with hydroxyl radical and produces a less reactive hydroperoxyl radical according to equation 21 **(Walling, 1975).**

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \qquad (21)$$

Also in oxidation reaction excess amount of H_2O_2 reacts with ferric ions yielding Fe(III)-hydroperoxy complexes **(Laat and Gallard, 1999)** which reduces the ferrous ions required for Fenton reaction. In the present study, H_2O_2 was varied between 0.05 and 0.25 mL/200mL for degradation of 50mgL^{-1} 2Cl4NP (200 mL) solution by keeping other conditions constant (pH 3, F.S. 0.1 gm). Fig. 23 depicts that maximum degradation of 93.56 % was achieved at 0.05 mL H_2O_2 and thereafter degradation decreased which may be due to above mentioned reasons.

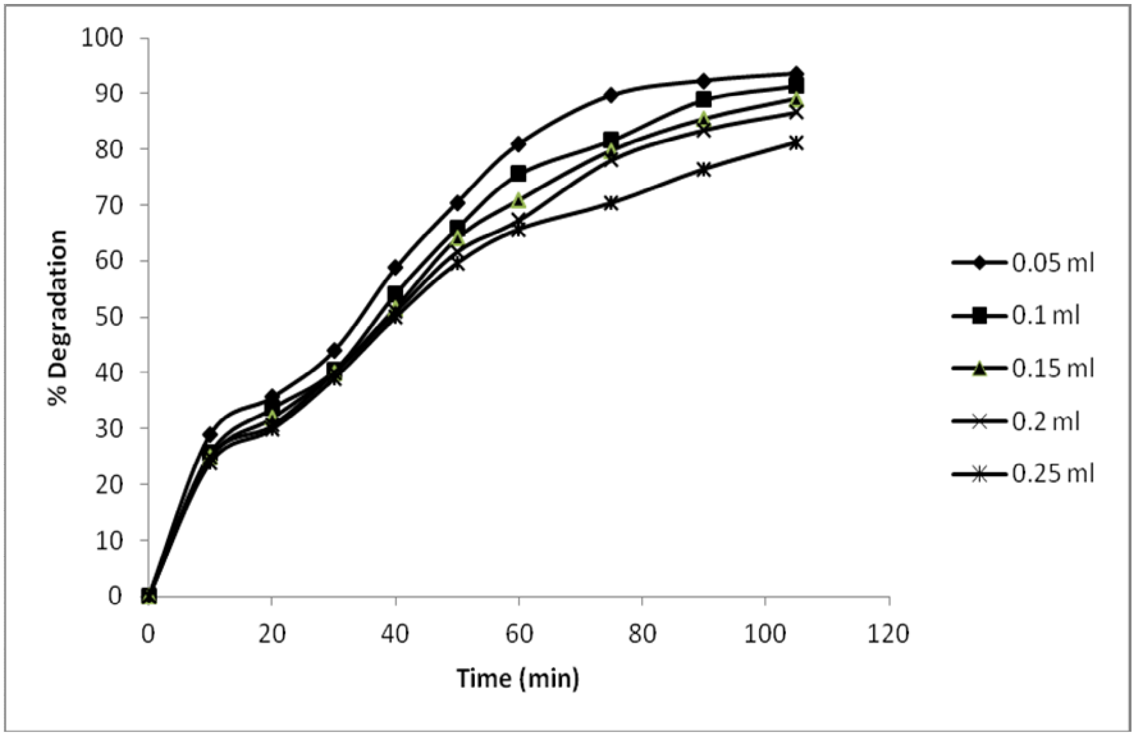

Figure 23: Percentage degradation of 2Cl4NP at varying concentration of H_2O_2.

5.4.3 Effect of Foundry Sand Concentration

In our study, FS was used as an alternative iron source as SEM-EDS analysis of FS confirmed the presence of iron which directs the oxidation of pollutants. To determine the optimum amount of FS, it was varied between 0.05 - 0.25 g at optimized conditions of 0.05 mL H_2O_2 and pH 3. It was observed that removal efficiency of 2Cl4NP increased with increase in addition of FS from 0.05 to 0.1 g and then started decreasing with further addition as shown in fig. 24. The reason for the initial increase in degradation of 2Cl4NP is the consumption of H_2O_2 by ferrous ions and thereby increasing the production of more hydroxyl radicals. While excessive ferrous iron (>0.1 gm) shows scavenging effect of hydroxyl radical thus reducing the degradation rate as depicted in reaction 22 **(Buxton et al., 1988).** Though after 60 min, degradation was similar for different amounts of sand (0.05-0.25 g) but we selected 0.1 g sand because rate of degradation is fast as compared to others and 97.19 % degradation was achieved in 105 min.

$$^{\cdot}OH + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \qquad (22)$$

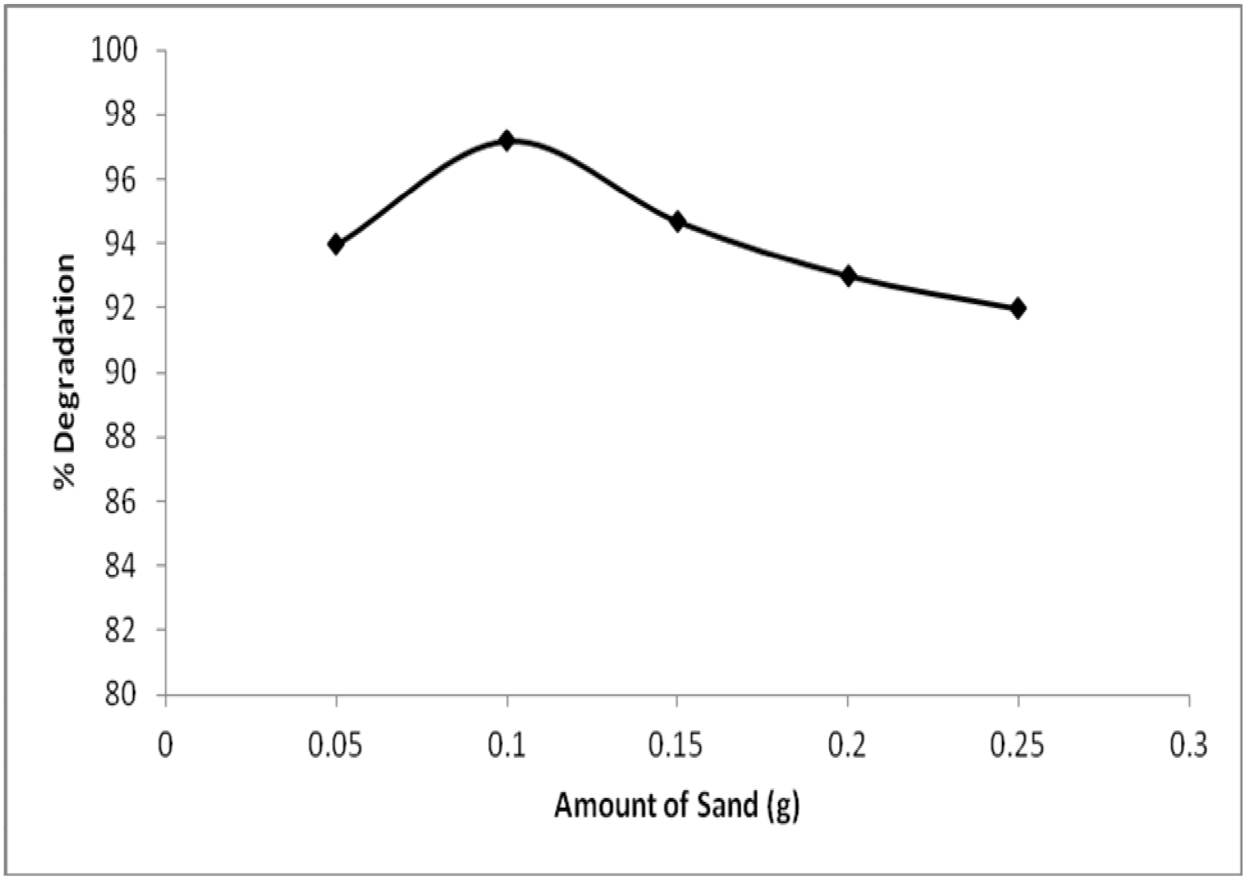

Figure 24: Percentage degradation of 2Cl4NP at varying concentration of Foundry sand (V=200 mL, pH=3, H_2O_2=0.05 mL/200mL).

5.4.4 Effect of initial concentration of 2Cl4NP

Pollutant concentration plays an important role in wastewater treatment. Hence the effect of variation of initial concentration of 2Cl4NP was studied keeping other parameters fixed pH 3, 0.1 gm FS, 0.05mL H_2O_2. Degradation increased with increase in concentration of 2Cl4NP concentration as shown in fig. 25 as 2Cl4NP concentration increased from 10 to 50 mgL^{-1}, degradation increased from 78.82 to 97.192 % in 105 min.

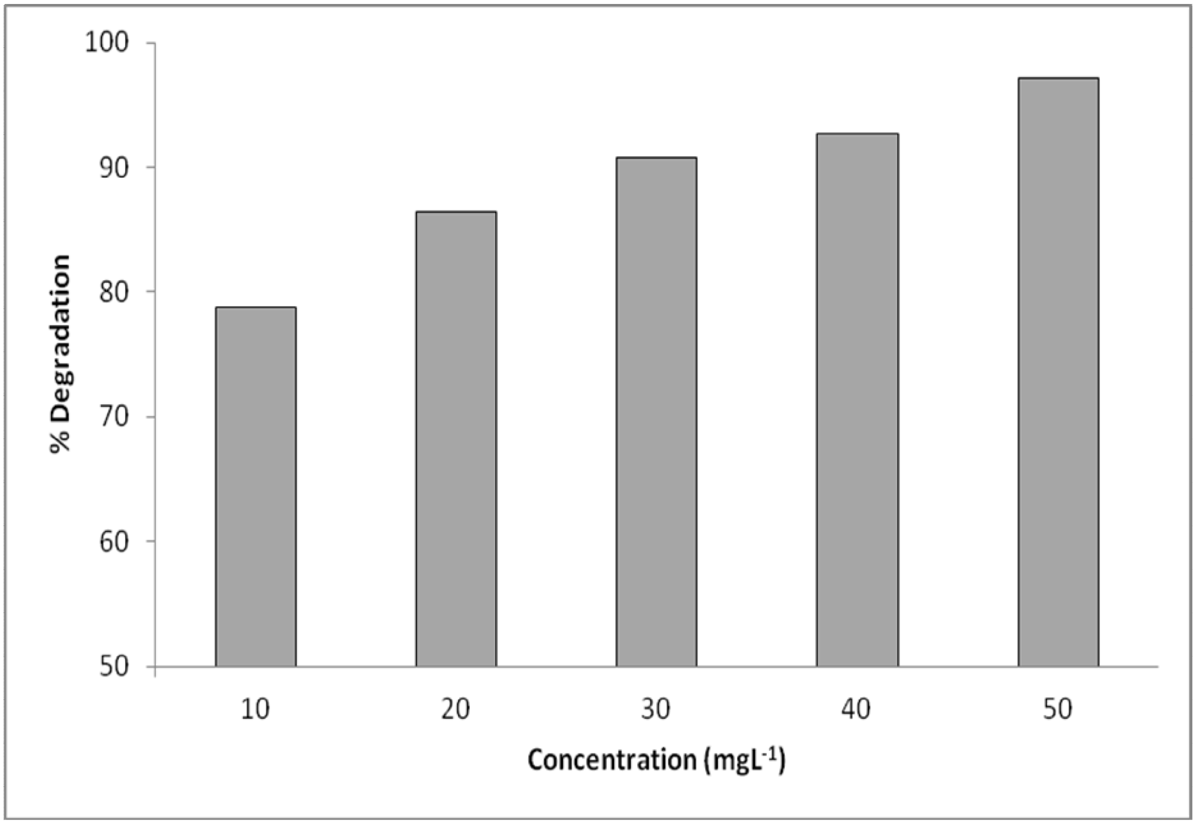

Figure 25: Percentage degradation of 2Cl4NP at varying concentration of 2Cl4NP (V=200 mL, pH=3, H_2O_2=0.05 mL/200mL, FS=0.1g).

5.4.5 Effect of Iron Leaching

Handling and disposal of FS is difficult and it adds other pollutants in water posing threat to the environment. Efforts are done to leach out iron from foundry sand in dissolved iron form to carry out photo-Fenton studies. In the present study iron was leached in water having pH 3. 0.1 g sand was dipped in 200mL distill water for 1 hr. After 1 hr it was filtered by blotting paper. Atomic Absorption Spectroscopy (AAS) analysis of the above solution revealed the presence of sufficient amount (as shown in table 4) of Iron and Aluminum which can be used in the solar photo-Fenton reaction as catalyst. The reaction was carried out in sunlight adding 0.05mL H_2O_2 to the above solution. 87 % degradation was achieved in 180 min as shown in fig.26.

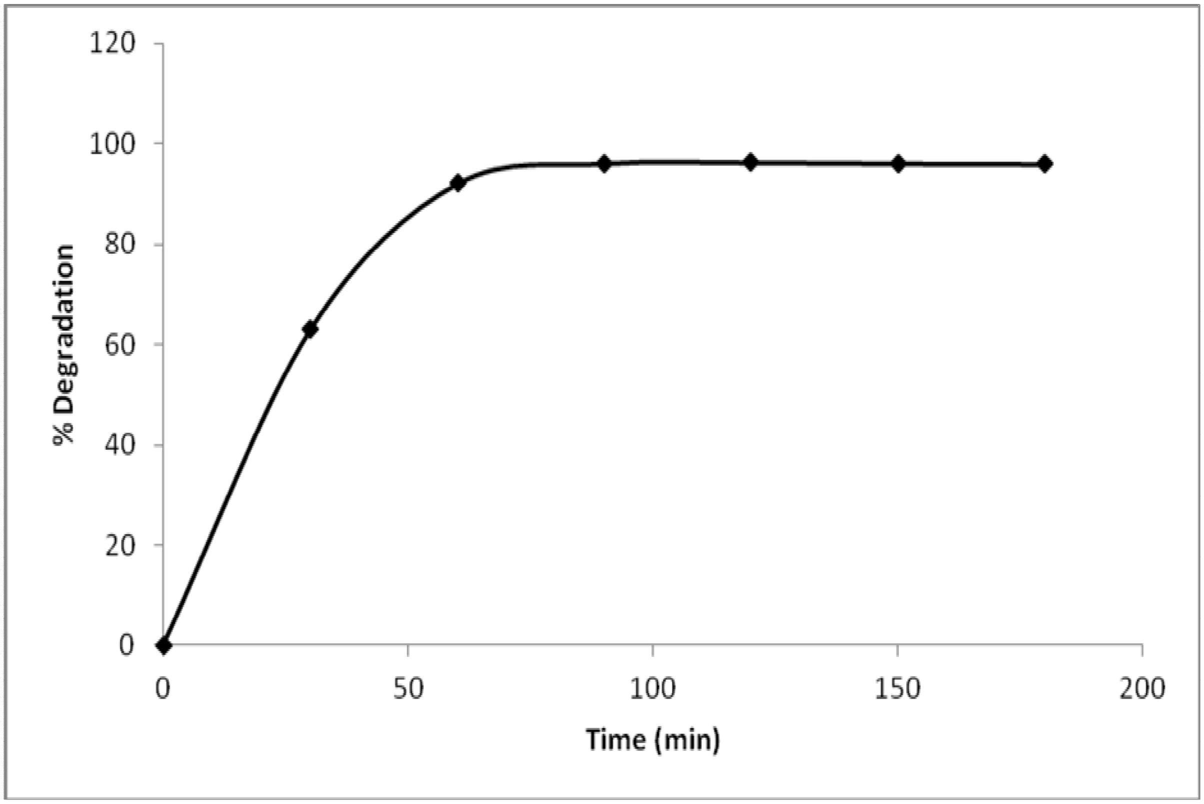

Figure 26: Effect of leached out iron from FS on 2Cl4NP degradation during photo-Fenton Process.

Table 4: AAS analysis of leached out water.

S. No.	Parameter	Unit	Results
1	**Iron as Fe**	**mg/L**	**0.26**
2	**Aluminum as Al**	**mg/L**	**<2.5**

The subsequent degradation of 2Cl4NP using FS as an alternative iron source in heterogeneous solar photo-Fenton process depicts the continuous use of iron present in FS which was cross confirmed by subsequent analysis (SEM-EDS) of FS. The reduction in composition of iron and aluminum confirmed their participation in photo-Fenton reactions.

5.5 Mineralization Studies

The mineralization of 2Cl4NP was evaluated in terms of reduction in COD. Transformation of all the carbon atoms into gaseous CO_2 and the heteroatoms to inorganic anions confirms the complete mineralization of pollutant **(Evgenidou et al., 2005).** Mineralization of the selected compound (2Cl4NP) was confirmed through HPLC analysis as peaks of the parent compound almost diminished in HPLC chromatograms after 75 min of treatment (fig. 27(b)) but the reaction continued to 2 h so that the other impurities/intermediates which may be present may be degraded which was confirmed through COD. Approximately 75% decrease in COD occurred after 2 h of treatment (fig. 27(a)).

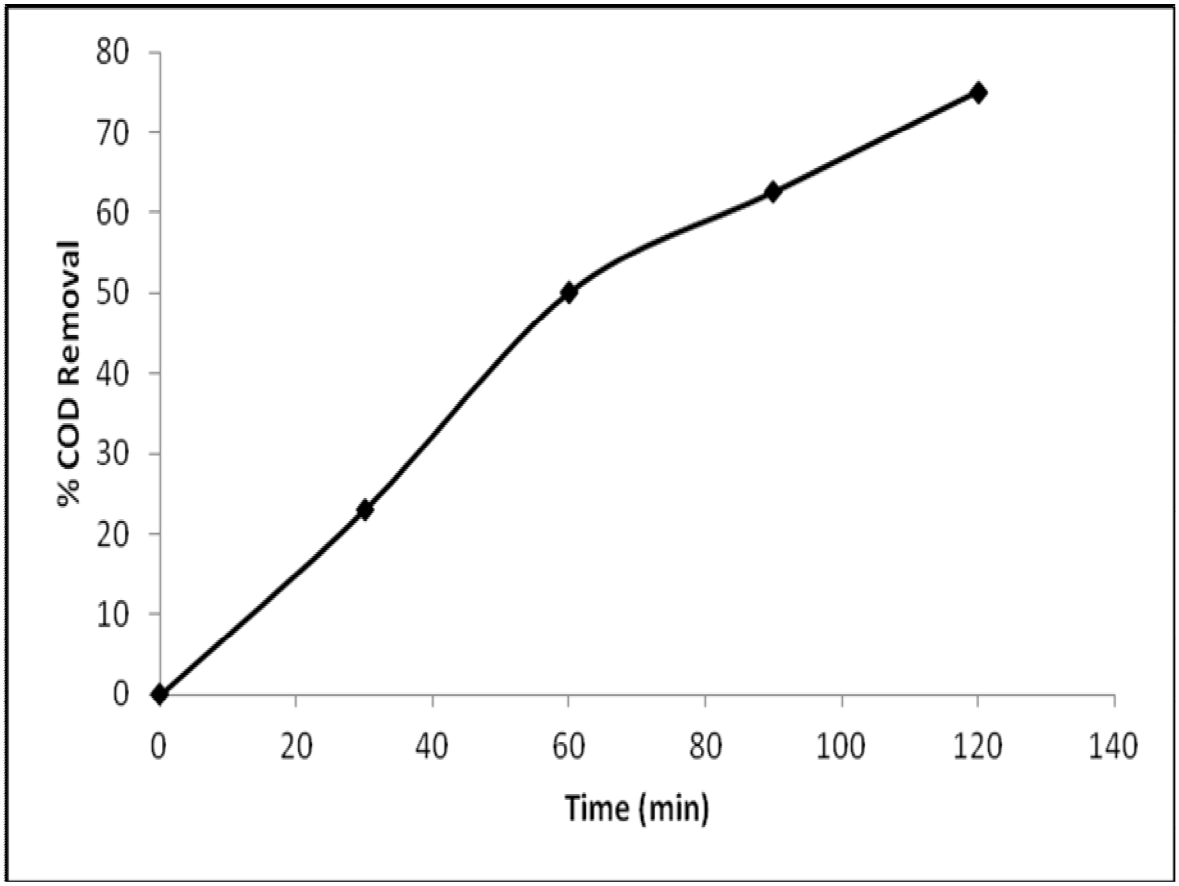

Figure 27(a): COD reduction during photocatalytic degradation of 2Cl4NP

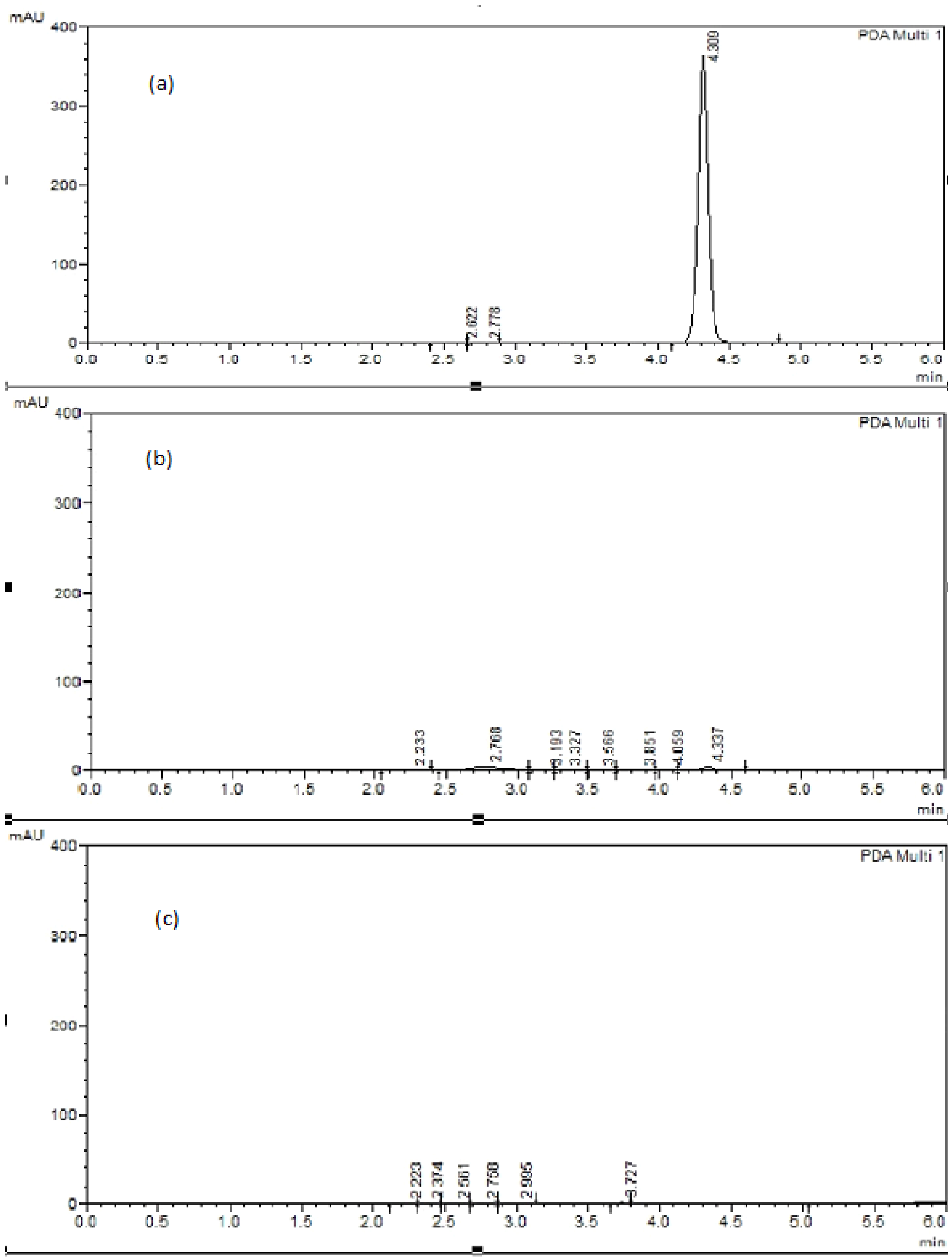

Figure 27 (b): HPLC chromatogram of (a) initial standard of 50 mgL^{-1} (b) after 15 min of treatment (c) after 75 min of treatment.

CHAPTER 6

CONCLUSION AND FUTURE ASPECTS

The photodegradation efficiency of heterogeneous photocatalysis using slurry, immobilized form and heterogeneous solar photo-Fenton process has been evaluated for the degradation of 2Cl4NP. The optimized values of operating parameters in case of TiO_2 photocatalysis were: TiO_2= 0.75 gL^{-1}, pH= 4, H_2O_2= 0.1 mL/200 mL and in case of solar photo-Fenton process the optimized conditions were: H_2O_2= 0.05 mL/200 mL, FS= 0.1 gm. Efficiency of cement and clay beads was checked. To the best of our knowledge this is the first reported study of using clay beads for immobilization of TiO_2. Foundry sand was employed as an alternative iron source in heterogeneous solar photo-Fenton reaction. Slurry photocatalysis yielded 97.19% degradation of 2Cl4NP in 210 min while 52% and 68% degradation of the compound was achieved in fixed-bed photocatalysis using clay and cement beads respectively and whereas in case of solar photo-Fenton process, 97.19% degradation was obtained in 105 min. The complete mineralization of 2Cl4NP was assured with 75 % reduction in COD as well as elimination of the parent compound peak in HPLC chromatograms.

In our study, both the techniques (heterogeneous slurry mode and fixed bed immobilization and use of alternate iron source in heterogeneous solar photo-Fenton process) have shown their potential in degrading bio-recalcitrant compound 2Cl4NP. Although slurry photocatalysis proved its worth for better degradation but for the commercial application immobilized photocatalysis have greater potential. With effective reactor designing, improved retention time, robust inert materials for immobilization, the technology can be developed and tested in field. This technology can be suggested to be incorporated in existing conventional treatment techniques as pre and post treatment options. They can also be employed as post treatment methods in biological treatments to remove odour and other trace components left after the treatment.

CHAPTER 7

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2. “Investgations on the use of Foundry Sand as alternative Iron source for studying degradation of fungicide Carbendazim using solar photo-Fenton.”. National Seminar on Sustainable Renewable Energy Generation- Current Scenario. Energy research centre, Punjab University, Chandigarh. March 20-21, 2015.