STUDIES ON PARAMETRIC OPTIMIZATION OF PENTACHLOROPHENOL USING BOX – BEHNKEN DESIGN

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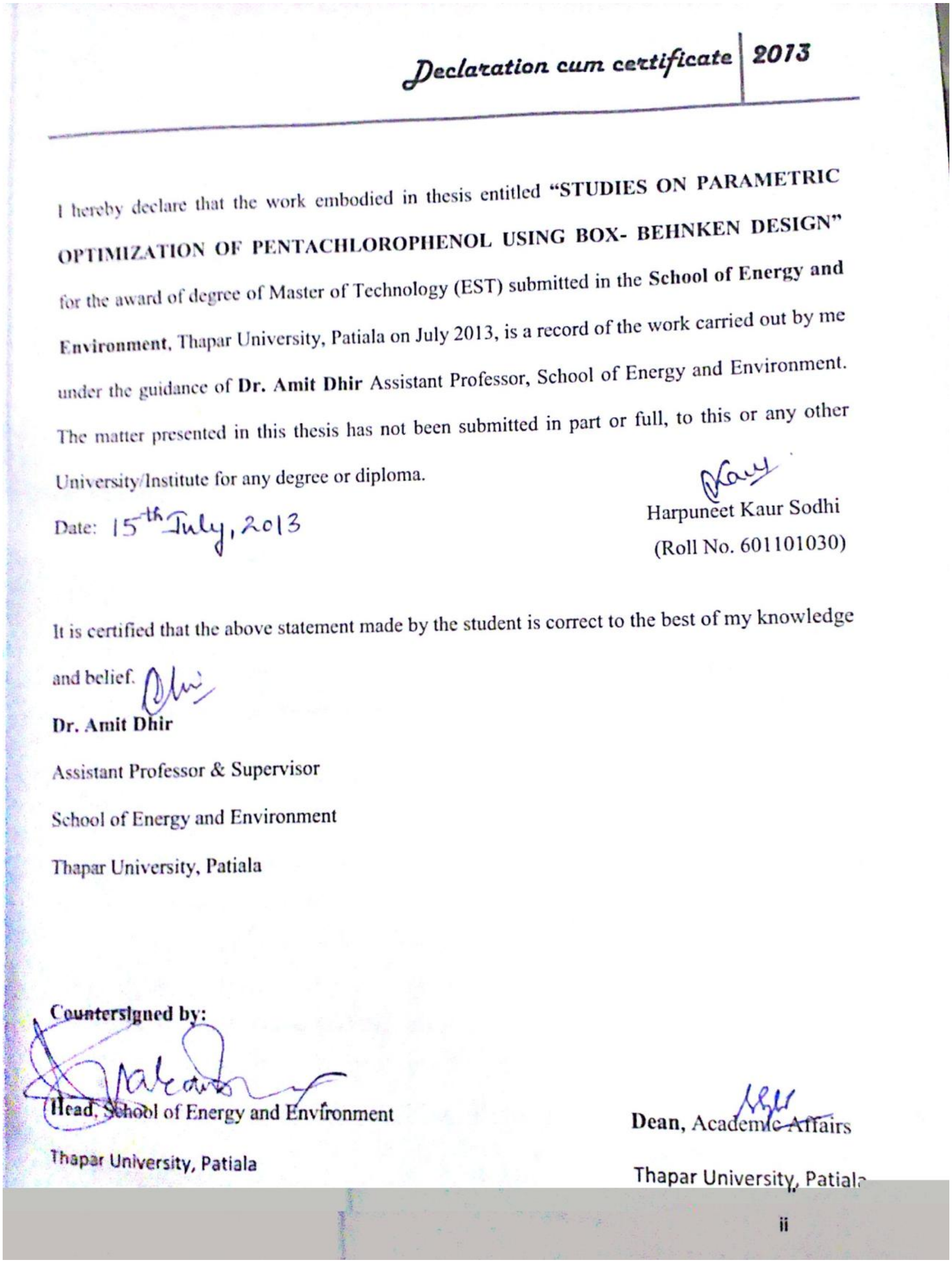

I hereby declare that the work embodied in thesis entitled **"STUDIES ON PARAMETRIC OPTIMIZATION OF PENTACHLOROPHENOL USING BOX- BEHNKEN DESIGN"** for the award of degree of Master of Technology (EST) submitted in the **School of Energy and Environment**, Thapar University, Patiala on July 2013, is a record of the work carried out by me under the guidance of **Dr. Amit Dhir** Assistant Professor, School of Energy and Environment. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

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Abstract

Due to the presence of biorecalcitrant organic contaminants in the environment resulting from the ever increasing industrial growth is of primary concern for the preservation of aquatic ecosystems. Biorecalcitrant compounds are basically non-treatable in conventional biological wastewater treatment plants, so the development of new technologies that pursue the degradation of such substances is of practical interest. Advanced oxidation processes (AOPs), which involves the in situ generation of highly potent chemical oxidants such as OH radicals, have emerged as an important class of technologies to accelerate the non selective oxidation and thus leads to the destruction of wide range of recalcitrant organic contaminants in wastewater which cannot be eliminated biologically. Among AOPs, heterogeneous photocatalysis has emerged as an efficient method for degrading the organic contaminants. Heterogeneous photocatalysis involves the acceleration of photoreaction in presence of semiconductor photocatalyst and UV irradiation. In the present study, Pentachlorophenol (PCP), which has been listed third in the priority pollutants list of EPA, was chosen as the model compound. PCP is an important industrial raw material frequently used in the manufacture of pesticide, herbicides and fungicides. The photocatalytic degradation of PCP (25 mg/l) was carried out in slurry mode in the specially designed photoreactor equipped with UV tubes at constant temperature. The UV/Vis Spectrophotometer was used for analyzing the concentration of PCP in solution at different time intervals during the experiment. The rate of degradation has been examined in terms of change in the absorbance at λ_{max} of 219 nm. The effect of varying various photocatalytic process parameters such as catalyst dose, pH, UV intensity and light source (UV/solar) has been investigated. 83.45% and 74.3% degradation efficiency was achieved after 6 hr under UV light employing ZnO and TiO_2 under optimized conditions (0.5 g/L ZnO; pH 8.0 and 0.5 g/L TiO_2; pH 8.0) respectively. The results demonstrated that ZnO exhibited better photocatalytic activity as compared to TiO_2 for the degradation of PCP. In order to minutely evaluate the effects of individual operating variables and optimization of process parameters, Box Behnken design of experiments was applied for the degradation of PCP with ZnO (25 mg/l). The variables examined in this study included ZnO dose, pH and time. The significant variables and optimum conditions were identified (ZnO dose .35 g/L, pH 9.5 and time 5.2) from statistical analysis of the experimental results. 89.5%

degradation efficiency was achieved under these conditions which were in agreement with the predicted value. The degradation of PCP shows better results in solar light under optimized conditions after 6 hrs with ZnO as compared to UV irradiation. The rate of degradation of PCP was also studied in terms of TOC. Maximum TOC reduction 86.89% was achieved on optimized conditions (0.5 g/l ZnO dose, pH 8 after 6 hrs) The results depicted that heterogeneous photocatalysis employing solar light can be efficiently and cost effectively used for the degradation of PCP.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

During the last 10 years, a drastic change in the development of the research activities devoted to environment protection has been recorded. The impact of rapid urbanization and industrialization especially among the developing countries like India, as they generate high amounts of residual wastewater, whose direct disposal to natural channels causes a considerable effect on the environment. This fact, together with the need to restore the water for new uses, makes practically essential for the purification of wastewater to achieve the desired degree of quality. Because of an increasing social and political concern on environment, the research field of water purification has been extensively growing in the last decades, comprising both polluted wastewaters and groundwater from seas, rivers and lakes, as water quality control and regulations against hazardous pollutants have become stringent in many countries. More recently, reflecting a new environmental conscience, the European Directive 2000/60/CE [EC Directive, 2000] stresses the need to adopt measures against water pollution in order to achieve a progressive reduction of pollutants. From past decades the persistent organic pollutants (POPs) are a matter of great concern, because they cannot be eliminated by the ordinary water or wastewater treatments [Metcalf & Eddy, 2003]. POPs have lipophylic and hydrophobic characters so they consequently bioaccumulate in fatty tissues of organisms and are capable of bioaccumulating or biomagnificating into food chains, reaching extremely high concentrations (in comparison to their environmental concentrations) on the top species [Baird, 1999]. Several of those substances have already been classified as priority substances for environmental monitoring. Dibenzodioxins, dibenzofurans, polychlorinated biphenyls and organo chlorinated pesticides join the list of priority organic pollutants of World Health Organization (WHO), United Nations Environmental Program (UNEP) and other Environmental Protection Agencies [Metcalf & Eddy, 2003]. Phenol and substituted phenols show toxicity values from moderate to highly toxic depending on the number, position and substitution nature. Some of the most toxic members of this class of compounds are the chlorinated and nitrosubstituted phenols that are used as pesticides and antibacterials (dinoseb, creosote, chlorinated phenol, p-nitrophenol). The principal use of the monochlorinated phenols is as intermediates in the synthesis of the higher chlorinated organics and certain dyes and pesticides. Chlorophenolic compounds (CPs) constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water

Act and by the European Decision 2455/2001/EC [EPA, 2002; Hayward., 1998 ; Keith and Telliard.,1979]. These are of great in environmental concern being raised due to their toxicity and non biodegradable nature [Fukushima and Tatsumi., 2001]. Because of its numerous origins, chlorophenols occur in all components of the natural environment. Chlorophenols that have moderate aqueous solubility are enriched in aquatic organisms towards the higher members of the food chain in the form of biomagnification (1) Once discharged into a receiver aquatic ecosystem, these compounds are quite persistent pollutants as they resist biodegradation (2) In addition to seepage from industrial effluents, chlorinated phenols also reach natural waters as chlorination residues of Cl_2-disinfection treatment (3) Chlorination of organic wastes, e.g., humic substances, in water may give rise to toxic products such as chloroform [Titus et al., 2005; Ahlborg et al., 1980]. Chlorophenolic compounds are recalcitrant to biodegradation and therefore persist in the environment. Because of their lipophobicity they can transport through cell membrane and bioaccumulate in aquatic organisms [Pedroza et al., 2007]. Despite their low concentration, these contaminants are a major health concern because of their extremely high endocrine disrupting potency and genotoxicity [Arques et al., 2007]. The presence of chlorinated compounds in aquatic environments has caused severe environmental pollution problems. Number of studies have been investigated for the degradation of CPs with photocatalyst such as 4-chlorophenol [Wang et al., 2008] and 2,4,6-trichlorophenol [Aal et al.,2009]. 2-chlorophenol and 2,4-dichlorophenol are typical phenolic substances has been used as an intermediate in making insecticides, herbicides, preservatives, antiseptics, disinfectants and other organic compounds [Gu et al.,2008]. 2,4,6-trichlorophenol is particularly of environmental interest owing to its mutagenicity and carcinogenicity [Lewis ., 2002]. Pentachlorphenol is on the US EPAs list of priority pollutants with the maximum concentration limit (MCL) of .001mg/l set for drinking water. Pure pentachlorophenol exists as colorless crystals. PCP has been widely used as a general herbicide and is very persistent in the environment. PCP can be released and transported into the atmosphere through evaporation and may contaminate surface and ground waters through dissolution and penetration in soil. The origin of PCP and its derivatives such as dioxin through thermal reactions in pesticide formulations are claimed to be probable human teratogens and carcinogens. In response, it has developed into a challenge to attain the effective removal of such persistent organic pollutants from waste water effluent to minimize the risk of pollution problems from such toxic chemicals and to enable its reuse. Consequently, considerable efforts have been devoted to develop a suitable purification method that can easily destroy these bio-recalcitrant organic contaminants. Some of the treatment technologies may be selective but slow to reasonable in destruction rate, or rapid but not selective, thus they require energy costs. Other treatment technologies can be limited by economic reasons or tendency to form harmful by-products. The conventional wastewater purification system in effective removal of many bio recalcitrant pollutants and strict pollution legislation is needed for the development of new treatment systems. As photocatlytic degradation involves number of parameters and multiple degradation pathways so its very difficult to evaluate them, due to its complexity and time consuming process, technique is used called as Response aurface methodology (RSM). RSM is a useful method in deciding the variables as well as in optimizing them. In the last decade, extensive experimental research is being carried out on the application of photocatalytic degradation of chlorophenols or phenols using RSM [Kansal et al., 2007].

1.2 TREATMENT TECHNOLOGIES

There is a growing interest in developing new and efficient cleaning technologies for environmental protection and remediation. Because of the increasing environmental awareness, several technologies for the degradation of such pollutants has drawn more attention viz biological, physical, chemical etc. For biological treatment, the main drawbacks are: slow reaction rates (long residence treatment), disposal of sludge and the need for strict control of proper pH and temperature, various other technologies are used for the removal of such biorecalcitrant organic pollutant [Danis et al., 1998].Various toxic and hazardous chlorinated compounds present in wastewater and surface water are difficult to be decomposed by conventional or biological methods, especially if they are present at low concentrations. Currently available water treatment technologies such as adsorption or coagulation simply concentrate the pollutants present by transferring them to other phases, but still remain and not being completely “eliminated” or “demolished” [Padmanabhan et al., 2006]. Other traditional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could produce toxic secondary pollutants into the ecosystem [Gaya and Abdullah, 2008]. These concentrated toxic contaminants are highly redundant and have been fretful worldwide due to the increasing environmental awareness and legislations.

Chlorination has been the most commonly and widely used disinfection process. The disinfection by-products generated from chlorination are mutagenic and carcinogenic to human health [Yang and Cheng, 2007; Lu et al., 2009; Coleman et al., 2005]. Because of the limitations of above discussed physiochemical biological treatment, there is a need to focus on environmental friendly technology for the treatment of such biorecalcirant compounds. One of the most promising techniques is advanced oxidation processes to achieve the complete degradation of biorecalcirant and hazardous organic compound.

1.3 ADVANCED TREATMENT PROCESSES

Apart from biological, thermal and chemical treatment, various other advanced treatment processes include electrons in electrochemical oxidation, chemical oxidation, reagents such as air or oxygen in wet oxidation and supercritical wet oxidation. Among these techniques advanced oxidation processes (AOPs) come out to be the promising method for field of study, which have been effective for the degradation of these bio-recalcitrant organic compounds. AOPs defined by Glaze et al, (1989) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (especially hydroxyl radicals) in adequate quantity to effect water purification by attacking the majority of organic matter. AOPs make use of different reacting system, involving the oxidation of bio-recalcitrant compounds by the production of hydroxyl radical (*OH) and these are highly reactive species/non-selective that are able to attack and destroy even the most persistent organic molecules which are not oxidized by the oxidants such as oxygen, ozone or chlorine [Fox et al., 1993; Sharma et al., 2011]. The oxidation potential of hydroxyl radical is 2.8 V relative (**Table-1.3**).

$$\text{AOPs} \longrightarrow {}^{*}\text{OH} \xrightarrow{\text{pollutant}} CO_2 \longrightarrow H_2O \longrightarrow \text{inorganic ions}$$

AOPs adaptability is also favored by the existence of various pathways to produce hydroxyl radicals, which enables a high compliance to any specific environmental remediation problem. The advanced oxidation process can degrade all types of organic compounds in water therefore; they are widely used in industrial wastewater remediation. Although oxidation can be complete, frequently a partial oxidation is sufficient to decrease the toxicity of the bio-recalcitrant compound enabling their final treatment by conventional biological treatment. The complete oxidation leads to mineralization and yields CO_2, H_2O and inorganic ions. Furthermore, the partial decomposition of non-biodegradable organic pollutants can lead to biodegradable intermediates. For this reason, combined AOPs as pre-treatments, followed by biological processes, are both cost efficient and extremely viable from an economic perspective [Canizares et al., 2009].

Table-1.3 Oxidation potential of most common oxidizing agents (Kansal et al., 2007)

Oxidizing agent	**Oxidation potential ,Volt**
Fluorine	3.06
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Molecular oxygen	1.23

1.4 HOMOGENEOUS AOPs

Homogeneous AOPs (single phase system) used to treat contaminated water involves the use of an oxidant to generate OH^* radicals in the presence of UV light, which attack the organic pollutants to start the reaction. The most important processes used for the homogeneous degradation are: hydrogen peroxide (UV/H_2O_2), hydrogen peroxide (H_2O_2), ozone, ultraviolet (H_2O_2 /O_3/ UV) and photo-Fenton (Fe^{+3}/ H_2O_2 /UV). The costs of UV radiation treatment processes depend to a huge extent on the absorption properties of the compounds to be removed. The compounds that absorb UV light at lower wavelengths are outstanding contenders for photo-degradation, such as in the case of pentachlorophenol and N-nitrosodimethylamine (NDMA) (Vogelpohl., 2007).

1.5 HETEROGENEOUS AOPs

The potential of heterogeneous photocatalysis has been demonstrated in studies originally reported by Fujishima and Honda (Fujishima & Honda, 1971; 1972). Heterogeneous photocatalytic oxidation process (two or more phase system) employing semiconductor as photocatalyst (TiO_2, ZnO,Fe_2O_3, CdS, GaP and ZnS) has established its efficiency in degrading a wide range of indefinite refractory organics into readily biodegradable compounds, and eventually mineralized them to harmless carbon dioxide and water. In this process, the combined action of semiconductor photocatalyst, an energetic radiation source and an oxidizing agent governs the destruction of organic compounds. Moreover, the process can be driven by solar, UV and visible light. In comparison to homogeneous processes, such heterogeneous catalysts have the advantage of sorting out the product with greater ease. A number of important features for the heterogeneous photocatalysis have extended their feasible applications in water treatment, such as; Ambient operating temperature and pressure, Complete mineralization of parents and their intermediate compounds without secondary pollution and Low operating costs.

1.5.1 MECHANISM OF PHOTOCATALYTIC OXIDATION PROCESS

A semiconductor is described by an electronic band structure in which the highest energy band is called as valence band (vb) , and the lowest empty band is called as the conduction band (cb) , are separated by a band gap (bg) .When a photocatalytic surface is illuminated by light (e.g – UV) with energy equal to or larger than the bandgap energy ΔE_{bg} , it excites the electrons in the valence band to the conduction band, resulting in the formation of a positive hole (p+) in the valance band and an electron (e–) in the conduction band. The principal mechanism of a semiconductor photocatalytic reaction as given (Fig-1.5) depicts that the positive hole oxidizes either pollutants directly or water to produce HO^* radicals, whereas the electron in the conduction band reduces oxygen adsorbed to photocatalyst. The mechanism described above can be represented by Eqs. (1) - (5) as shown below;

$$\text{SC (photocatalyst)} \longrightarrow e^- + h^+ \quad (1)$$

$$e^- + O_2 \longrightarrow O_2^- \quad (2)$$

$$p^+ + \text{Organic} \longrightarrow CO_2 \quad (3)$$

$$p^+ + H_2O \longrightarrow HO^* + H^+ \quad (4)$$

$$HO^* + \text{Organic} \longrightarrow CO_2 \quad (5)$$

In the photocatalytic degradation of the pollutants, when the reduction process of oxygen (Eq. (2)) and the oxidation of pollutants (Eq. (3) and (4)) do not proceed simultaneously, there is an electron accumulation in the conduction band, thereby causing a recombination of electron and positive holes. Therefore, efficient consumption of electrons is essential to promote photocatalytic oxidation. The most important and fundamental elements for a successful photocatalytic system are the catalyst, the light source and the reactor configuration.

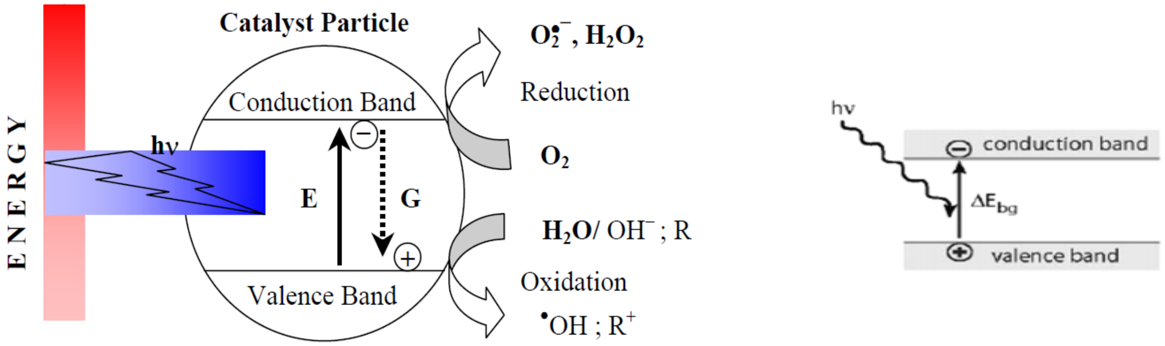


Fig 1.5 Schematic representation of the mechanism of photocatalytic activity (photochemical activation and elelctron-hole formation) [Ahmed et al., 2011].

1.5.2 PHOTOCATALYST

A broad range of semiconductors may be used for photocatalytic oxidation of organic pollutants, such as TiO_2, ZnO, ZnS and CdS. Among these, TiO_2 has received the greatest interest in research of photocatalysis technology. TiO_2 is an ideal photocatalyst also used as white paint pigment, as sun blocking material or as in different applications such as ceramics/glass, because it has; photoactivity, biological and chemical inertness, stability towards photocorrosion, suitability towards visible or near UV light, low cost, and lack of toxicity [Bhatkhande et al., 2001]. ZnO has been reported to be a suitable alternative to TiO_2 as far as band gap energy is concerned [Richard et al., 1992]. The biggest advantage of ZnO in comparison with TiO_2 is that it absorbs over a larger fraction of UV spectrum and also latter has larger quantum efficiency [Shinde et al., 2011]. ZnO has emerged to be a more efficient catalyst concerning water detoxification because it generates H_2O_2 more efficiently [Dindar et al., 2001], with high reaction and mineralization rates [Poulios et al., 1999]. Also, it has more number of surface active sites with high surface reactivity [Pall et al., 2002]. Other semiconductor (e.g. CdS or ZnS) absorb larger fraction of solar spectrum than TiO_2 and can form chemically activated surface bond intermediates. TiO_2 is the most active photocatalyst under the photon energy of 300 nm< λ< 390 nm and remains stable after the repeated catalytic cycles, whereas Cds or GaP are degraded along to produce toxic products [Malato et al., 2009].

1.5.3 FACTORS AFFECTING PHOTOCATALYTIC PROCESSES AND NEED FOR OPTIMIZATION

Optimizing refers to improving the performance of a system, a process, or a product in order to obtain the maximum benefit from it [Araujo et al., 1996] .The efficiency of a photocatalytic reaction depends on a number of factors, which manage the performance of photocatalysis. Initial concentration of pollutant, photocatalyst concentration, pH, volume of solution, irradiation time, light intensity, irradiation wavelength, temperature, geometrical parameters of the experimental setup and multiple degradation pathways are the parameters that can be mentioned. Due to the difficulty and diversity of influencing factors, it is not easy to evaluate the relative significance of several affecting factors, especially in the presence of complex relations. In the most recent studies, the conventional optimization technique is called as one-variable-at-a-time were tested for evaluating the influence of operating factors on the photocatalytic process efficiency. Its major disadvantage is that it does not include the interactive effects among the variables studied. As a consequence, this technique does not depict the complete effects of the parameter on the response [Lundstedt et al., 1998]. Another disadvantage of the one-factor optimization is the increase in the number of experiments necessary to conduct the research, which leads to an increase of time and expenses as well as an increase in the consumption of reagents and materials. To overcome this problem multivariate a technique is used in analytical optimization is response surface methodology (RSM). The purpose of RSM is to introduce statistically designed experiments to scientists who conduct the experiments for the purpose of making inferences from data. To achieve this goal, statistical considerations for preliminary planning of experiments, standard statistical designs that may be used for experiments and the basic logic for using these designs are emphasized. It is a common but major error to view statistics as a tool to be used only after the experiments are completed.

1.6 RESPONSE SURFACE METHODOLOGY (RSM)

Response surface methodology (RSM) is a collection of statistical and mathematical methods that are useful for the modeling and analyzing engineering problems. RSM allows an appropriate design of the experiments, which helps to decrease the number of runs. In addition, the modeling of the system facilitates the interpretation of multivariate phenomena and is valuable tool for scaling up [Braun et al., 2007]. In overall, it can be interpreted that a multi-variable (MV) optimization approach is actually required to optimize a photo-reactor system as parameter interface might exist. Parameter interfaces refer to the relationship between operating parameters such as TiO_2 loading on pH or pH on

The design procedure of response surface methodology is as follows:

- Designing of a series of experiments for adequate and reliable measurement of the response of interest.
- Developing a mathematical model of the second order response surface with the best fittings.
- Finding the optimal set of experimental parameters that produce a maximum or minimum value of response.
- Representing the direct and interactive effects of process parameters through two and three dimensional plots.

If all variables are assumed to be measurable, the response surface can be expressed as follows:

$$R_0 = f(x_1, x_{2.....}x_k) \qquad (1)$$

The objective is to optimize the response variable R_0. It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surface. Two important models are commonly used in RSM, including the first-order model (Equation (2)) [Khuri et al., 2010]

$$R_0 = \beta_0 + \sum_{i=0}^{K} x_i \, \beta_0 + \text{€} \qquad (2)$$

Usually a second-order model is utilized in response surface methodology in Equation (3)

$$R_0 = \beta_0 + \sum_{i=0}^{k} x_0 \, \beta_0 + \sum_{i=0}^{k} x_i^2 \, \beta_{ii} + \sum_{i=0}^{k} x_i \, x_j \, \beta_{ij} + \text{€} \qquad (3)$$

Where R_0 is the predicted response output, i, j are linear, quadratic coefficients, and €

is a random error respectively. The parameters of β and k are regression coefficient and the number of parameters studied in the experiment respectively, and x_i, x_j ($i = 1, 4$; $j = 1, 4$, $i \neq j$) represent the number of independent variables in the study. The β coefficients, which should be determined in the second order model, are obtained by the least square method. The mathematical models were evaluated for each response by means of multiple linear regression analysis. As said previous, modeling was started with a quadratic model including linear, squared and interaction terms. The significant terms in the model were found by analysis of variance (ANOVA) for each response. Significance was judged by determining the probability level that the F-statistic calculated from the data is less than 5%. The model adequacies were checked by R^2, adjusted- R^2, predicted- R^2 and prediction error sum of squares (PRESS). A good model will have a large predicted R^2, and a low PRESS. After model fitting was performed, residual analysis was conducted to validate the assumptions used in the ANOVA. This analysis included calculating case statistics to identify outliers and examining diagnostic plots such as normal probability plots and residual plots.

Maximization and minimization of the polynomials thus fitted was usually performed by desirability function method, and mapping of the fitted responses was attained by using computer software such as Design Expert [Raissi et al., 2009].

The second-order model is the most-frequently used approximating polynomial model in Response surface methodology. The most common designs for the second-order model are the 3*k* factorial, Doehlert, Box–Behnken and central composite designs (CCDs). These symmetrical designs differ from one another with respect to their selection of experimental points, number of levels for variables and number of runs and blocks. Adequacy of the proposed model is revealed using the diagnostic checking tests provided by analysis of variance (ANOVA).

CHAPTER 2

REVIEW OF LITERATURE

As recalcitrant organic pollutants keep on increasing in air and wastewater streams, environmental laws and regulations become more stringent and as a result the development of newer eco-friendly methods of destroying these pollutants became an imperative task. Finally, among traditional techniques the so called “Advanced Oxidation Process” has been developed, which usually operates at or near ambient temperature and pressure. Research activities centered on AOPs for the destruction of synthetic organic species which are resistant to conventional treatment methods. AOPs make use of different reacting system, involving the oxidation of bio recalcitrant compounds by the production of hydroxyl radical (OH^*) and these are highly reactive species/non-selective that are able to attack and destroy even the most persistent organic molecules which are not oxidized by the oxidants such as oxygen, ozone or chlorine [Fox et al., 1993; Sharma et al., 2011; Blake et al., 2001]. The most attractive feature of AOPs is that this highly potent and strongly oxidizing radical allows the destruction of a wide range of organic chemical substrate with no selectivity. Among AOPs, heterogeneous photocatalysis has proved to be of real interest as an efficient tool for degrading both aquatic and atmospheric organic contaminants [Schiavello, 1988; Serpone 1997; Chen et al., 1997; Alhakimi et al., 2003; Guillard et al., 2003; Lathasree et al., 2004;Guillard et. al., 1999]. Heterogeneous photocatalysis involves the increase of rate of photoreaction in presence of semiconductor photocatalyst. In the most recent studies, only traditional one-factor-at-a-time experiments were tested for evaluating the influence of operating factors on the photocatalytic process efficiency. This technique is not only time and work demanding, but also completely lacks representation of the effect of interaction between different factors. Response surface methodology (RSM) is an extensively used technique for modeling and optimization of the photocatalytic treatment processes of water and wastewater. This methodology not only estimates linear interaction and quadratic effects of the factors on the response, but also provides a prediction model for the response at the range of the variables studied and the optimum conditions to achieve the highest performance. The present chapter reviews the work done in the field of heterogeneous photocatalytic degradation of chlorophenols with special emphasis on pentachlorophenol and optimization of the process parameters by RSM.

2.1 Photocatalytic degradation of chlorophenolic compounds

Andreozzi et al, (1999) observed that pollutants not amenable to biological treatments due to this are not totally degraded, so there is need to focus more on efficient treatment than those conventional purification processes. Numerous studies of photocatlytic decomposition of CPs using semiconductors in aqueous heterogeneous system have been considered. Jardim et al, (1997) shown the feasibility of heterogeneous photoctalysis using TiO_2 in the detoxification process, particularly when chlorinated phenols are the target compounds. Ku and Hsieh, 1992 observed almost complete degradation of 2,4-dichlorophenol in aqueous solution under UV light in few hours of irradiation time and it was reported that the degradation rate was influenced by the catalyst loading and pH of the solution.

Bandara et al, (2001) reported that the photocatlytic degradation of mono, di and trichlorophenols with TiO_2 and iron oxide aqueous suspensions and explained that the absolute mineralization of chlorophenols was seen with TiO_2 whereas with iron oxide, only fractional mineralization was observed.

Antonaraki et al, (2002) studied the photocatlytic degradation of all chlorophenols in the presence of H_2O_2 or polyoxometallate (POM) photocatalyst under UV and visible light in aqueous phase.

Hugul et al, (2002) observed that the number of chlorophenols, specifically 2-chlorophenol, 2,4,-dichlorophenol and 2,4,6-trichlorophenol, were degraded in aqueous solution by using TiO_2 as photoactivated catalyst under UV irradiation. The organic-bound chlorine was converted into the environmentally harmless inorganic chloride. For catalyst doses between 0.1 and 0.5g/1 the reaction mechanisms are revealed.

Barakat et al, (2005) tested the effect of catalyst loading on the photocatlytic degradation of 2-CP. The degradation reached a maximum value of 93.4% with catalyst dose and degradation efficiency increases with increase in catalyst dose.

Parida and Parija, (2006) examined the effect of initial substrate concentration on the photocatlytic degradation of phenol under sunlight, visible and UV light, respectively. With the increase in the substrate concentration, the degradation efficiency decreased from 100 % to 60% under solar irradiation. Under UV light, the degradation was reported to decrease from 94 % to 52% with increasing initial concentration of phenol. The degradation was found to decrease from 95 % to 50% under visible light.

Kansal et al, (2009) studied the photocatalytic degradation of 2,3-dichlorophenol(2,3-DCP) in a batch reactor under UV light in slurry mode using titania P-25 as a photocatalyst and H_2O_2/NaOCl as oxidants. The variables studied include catalyst dose, solution pH, oxidant concentration and initial substrate concentration. The rate of degradation was studied in terms of changes in the concentration of the pollutants and reduction in chemical oxygen demand. The degradation rate of (2,3-DCP) was favorable at acidic pH with both oxidants. The optimum value of catalyst dose and oxidant concentration was found to be 0.75 g/L and 10 mM.

Dixit et al, (2010) studied the photochemical oxidation of phenol and chlorophenol aqueous solutions in a batch recycle photochemical reactor using UV irradiation, hydrogen peroxide and TiO_2 (as photocatalyst). The results indicated maximum 74.6% and 79.8% degradation of phenol and chlorophenol, respectively within 90 minutes of radiation time.

Ba-Abbad et al, (2010) investigated that the photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution was carried out in batch process with ZnO prepared by sol-gel method. The photocatalyltic activity of the ZnO was evaluated by photocatalytic degradation of initial concentration 50 mg/l of 2,4-dichlorophenol by observing molecular absorbance at $\lambda = 285$ nm. Optimum value of catalyst dose was found to be 2 g/l. The experimental results showed that the photocatalytic degradation efficiency of 2, 4-dichlorophenol for 1 h irradiation time was up to 98 %.

Abdullah et al, (2010) examined the destruction of aqueous 2,4-dichlorophenol in ZnO suspension irradiated by low wattage UV light at 299 K. The operating variables studied include initial 2,4-dichlorophenol concentration, photocatalyst doses and pH. The results showed that at 1.5 g/l feed concentration of ZnO and 50 mg/L initial 2,4-dichlorophenol level, a complete degradation was achieved in 180 min.

Kansal et al, (2012) observed that photocatalytic degradation of 2,6-DCP in aqueous phase using titania (PC-105) as a photocatalyst under UV light . The rate of degradation was estimated from residual concentration spectrophotometrically. Various parameters affecting the degradation process viz. catalyst dose, pH, initial substrate concentration and time were investigated in order to obtain their optimum values. The maximum degradation of 2,6-DCP was achieved with 1.25 g/l catalyst dose at pH-4.

Dhir et al, (2012) reported the effect of major process parameters such as catalyst dose ,pH, oxidant concentration and source light (UV/Solar) for the photocatalytic degradation of 4-Chlorocatechol using AOPs (UV/ TiO_2 /NaOCl and UV/ZnO) 99.2 and 91.2 % degradation was observed with ZnO respectively.

Alimoradzadeh et al, (2012) investigated the photochemical oxidation of 4-chlorophenol in aqueous solutions in a batch reactor using UV irradiation, hydrogen peroxide and nickel oxide. The efficiency of the system was evaluated with respect to reaction time, pH, intial concentration of reactants, catalyst load, light intensity, and the reaction rate constant. The results showed that the optimum conditions (the complete 4-chlorophenol removal (100%) at 60 min) were obtained at a neutral pH, with 0.2 mol/l H_2O_2, and 0.05 g/l of nickel oxide. The results of mineralization and chloride ions indicated that dechlorination was better accomplished but more time was required to completely mineralize 4-chlorophenol into water and carbon dioxide.

Ba-Abbad et al, (2012) reported the photocatalytic activity of TiO_2 nanoparticles (where nanoparticles were prepared by sol gel method) was tested by the degradation of chlorophenols namely, 2-chlorophenol (2-CP), 2, 4-dichlorophenol (2,4-DCP) and 2, 4,6-trichlorophenol (2,4,6-TCP) within range from 50 to 150 mg/1 initial concentrations under direct solar radiation. The results of photodegradation, 99, 98 and 92 % was obtained for 50 mg/1 of 2-CP, 2,4-DCP and 2,4,6-TCP receptively after 90 min irradiation time at pH of 6. At the same time, the efficiency value was decreased with initial concentration more than 50 mg/1.

2.2 Photocatalytic Degradation of Pentachlorophenol (PCP)

Both biological and chemical remediations were used for degradation of PCP. Among scores of chemicals tested, PCP ranked among the most toxic and recalcitrant compounds to activated sludge [Lee et al., 1992]. It is a highly toxic contaminant that damages the human immune system and reproductive system. Additionally when PCP exposed to environment can be decomposed to even more toxic compounds such as polychlorinated dibenzodioxins and dibenzofurans. To remove PCP from environment many conventional techniques, involving, as biodegradation, direct photolysis but photocatlytic degradation is an effective method to eliminate PCP from aqueous solution. Barbeni et al, (1985) performed the photodegradation of PCP by the use of different semiconductors (such as TiO_2, ZnO, CdS, WO_3 and SnO_3) and found

TiO_2 to be the most strong among all the diverse semiconductors photocatalyst. Villasenor et al, (1998) observed the photocatalytic degradation of PCP using ZnO as photocatalyst. The degradation was studied in a conventional photoreactor using 30 ppm of pentachlorophenol.

Jung et al, (2001) investigated the photocatalytic degradation of PCP by using chemical vapour deposition method where degradation was observed with TiO_2 thin films were prepared by sol gel method and was coated on some supporting material. Photodegradation of PCP was improved by CVD method and by coating material which gives best support.

Gunlazuardi et al, (2005) studied the photocatalytic degradation of PCP in aqueous solution employing immobilized TiO_2 on titanium metal. TiO_2 film was prepared via a deep coating in a sol–gel system calcinated at 525 ^{0}C. Two catalysts sheets (5 cm×5 cm, each) were put in a batch reactor containing 10 ppm PCP and irradiated by a UV black light. The occurrence of PCP degradation was indicated by decrease in pH, increase of conductivity, and formation of chloride ion.

Lin et al, (2006) reported that metal-doped TiO_2 was an effective catalyst for the photocatalytic degradation of PCP. Ag and Pd modified TiO_2 were shown to have improved photocatalytic activity for the degradation of p-chlorophenol compared with TiO_2 degussa P-25 which was coupled with better charge separation and therefore, to slower recombination [Kirilov et al., 2006]. In comparison to Ag-TiO_2 exhibited seven times higher photodegradtion rate of PCP in the presence of perxomonosulfate while 2.7 times higher in the perxodisulfate [Ahmed et al., 2010].

Yang et al, (2008) observed the degradation of pentachlorophenol (PCP) in the microwave-assisted photocatalysis (MAPC) process was faster than other processes including microwave-assisted direct photolysis (MADP), microwave process alone (MP) and dark process (DP). The photocatalytic activity of F-Si-TiO_2 (FST) modified catalyst is much higher than that of Si-TiO_2, F-TiO_2 and P-25 titania. It may be attributed to its strong capacity of absorption to the UV–Vis irradiation and more hydroxyl radical on surface of FST. In MPAC process, 40mg/l PCP was completely degraded in 20 min and its corresponding mineralization efficiency was 71%, the pH of solutions decreased from10.3 to 6.47 and the dechlorination was completed in 12 min.

Garbellini et al, (2010) reported degradation of PCP using a boron-doped diamond. Different decay levels of the PCP spectrum bands in 220, 251 and 321 nm, were observed after application of ultrasound without electrochemical process (18.1, 17.7 and 19.8 %), silent electrolyses (29.3, 71.6 and 70.8 %), pulsed sonoelectrolysis (31.0, 75.1 and 76.3%) and sonoelectrolyses (39.2, 80.0 and 82.6 %) respectively. For silent and sonoelectrolyses processes, cleaning/reactivation of the BDD surface by acetonitrile and/or electrochemical treatment was necessary. The pulsed sonolectrolysis were carried out purposely without cleaning/reactivation of the surface. The results showed greater PCP degradation for insonated studies than those obtained for the silent electrolyses, due to the increase of mass transport, minimization of the electrode fouling and the combined generation of hydroxyl radicals by both ultrasound and the polarized BDD surface.

2.3 Optimization of process parameters by Response surface methodology (RSM)

RSM is a useful method in the selection of such factors as affects the response with statistical significance and also to establish regression models. RSM can be useful for impinging on the desired target, and for optimizing a response. This also helps in making a process strong. RSM consists of various statistical techniques, for example Box- Behnken design (BBD) for model building and model exploitation. The Box–Behnken design was also employed by Annadurai et al, (2000) to study the effect of different variables on the photocatalytic decolorization of Congo red under sunlight irradiation using ZnO catalyst. Four variables, including the dye concentration, weight of catalyst ZnO, pH and reaction time, have been chosen to identify the considerable effects and interactions in the batch studies. According to the design selected, 29 experiments have been carried out and a second-order polynomial regression model has been developed using the experimental results. They have found that the photodecolorization potential of ZnO is strongly affected by the variations in the dye concentration, weight of catalyst ZnO, pH and reaction time. The experimental values were in good agreement with the predicted values and the R^2 value was found to be 0.9982. The maximum percentage of photodecolorization of 97% has been achieved in optimum conditions of the variables, including the dye concentration of 0.05 g/l, ZnO 0.16 g/l, pH 7.0 and reaction time of 2.0 h.

Kansal et al, (2007) applied the response surface methodology to investigate the performance of photocatalytic process for degrading catechol using Titanium dioxide and Zinc Oxide catalysts. The factors investigated included catalyst dose, pH and amount of oxidant. The experimental results indicated that the optimal conditions for the complete degradation of catechol were TiO_2 2.0 g/l, pH 6.0 and oxidant amount 0.95 ml.

Ray et al, (2009) selected a four factor three level Box-Benkhen design (BBD) todepict the photocatalytic degradation of phenol in an aqueous media and studied the effect of four process variables i.e. Titanium dioxide (TiO_2) catalyst size, TiO_2 concentration, dissolved oxygen (DO) concentration and phenol concentration. A maximum degradation rate (0.083 mi^1) with conditions set at 9.091 nm TiO_2 particle size, 1.0 g/l TiO_2, 31.0 mg/l DO and 40 mg/l phenol was obtained.

Kansal et al, (2009) made an attempt to study the photocatalytic degradation of 2,4-DCP under UV light using titania P-25 (surface area 50 m^2/g) as a photocatalyst and sodium hypochlorite as an oxidant. The variables investigated include catalyst dose, pH and oxidant concentration. The rate of degradation was studied in terms of changes in concentration of the pollutant and reduction in chemical oxygen demand and the optimal values of operational parameters leading to 2,4-DCP abatement were obtained by using response surface methodology

Yeber et al, (2010) performed factorial 2^n design to obtain the best experimental conditions to efficiently remove the compounds from the solution, using time and oxidant concentration as experimental variables. The initial concentration of both compounds was 100 ppm, and we obtained 90% dichlorophenol removal, with a rate constant of 0.0386 min^{-1}. Degradation of azo dye was more efficient reaching 98%, with a rate constant of 0.0908 min^{-1}. In both cases, the optimal time for reducing the maximum concentration was 60 min of irradiation. Total organic carbon (TOC) reduction was analyzed to determine the efficiency of the $UV/K_2S_2O_8$ process in mineralization, where we obtained 90% TOC reduction for both organic compounds.

Central composite design, an experimental design for response surface methodology (RSM), was used for the modeling and optimization of the phenol degradation. Analysis of variance (ANOVA) indicated that the proposed quadratic model was in agreement with the experimental case with R^2 and R^2_{adj} correlation coefficients of 0.9760 and 0.9544, respectively.

Accordingly, the optimum conditions for phenol degradation were a photocatalyst loading of two layers, initial phenol concentration of 34.44 mg/l and H_2O_2 concentration of 326.90 mg/l. The TiO_2/GAC was used for five cycles with phenol degradation efficiency still higher than 90%. Finally, the phenol that remained adsorbed on GAC was able to migrate to TiO_2 and then photocatalytically be degraded. [Sin et al., 2011].

Jafarzadeh et al, (2011) applied the Response surface methodology (RSM) using D-optimal design to optimize the photocatalytic degradation of phenol by new composite nanocatalyst (TiO_2/Perlite) and studied the effect of seven factors (initial pH, initial phenol concentration, reaction temperature, UV irradiation time, UV light intensity, catalyst calcinations temperature, and dosage of TiO_2/perlite) on phenol conversion efficiency. The results demonstrated that the optimum process conditions were initial pH 10.7; initial phenol concentration 0.5 mM; reaction temperature 27^0C; UV irradiation time 6.5 h; UV light intensity 250W; catalyst calcination temperature 600^0C; and TiO_2/ perlite dosage 6 g/l.

Hasan et al, (2011) explored the efficient, faster and economical operating conditions for phenol removal by investigating four parameters namely the concentration ratio of hydrogen peroxide to phenol - ((H_2O_2):(Phenol)), mass ratio of hydrogen peroxide to ferrous ions - ((H_2O_2):(Fe^{2+})), initial phenol concentration - ($[Phenol]_0$) and reaction time - (t_r). The mineralization was effectively achieved within 20 min for the range of concentrations investigated. The optimum conditions for the process were ratios of 6 and 15 for [H_2O_2]: [phenol] and [H_2O_2]: [Fe^{2+}], respectively.

Kansal et al, (2012) studied the photocatalytic degradation of 4-chlorophenol (4-CP) in a batch reactor under UV light of 120 W and wavelength 365 nm in slurry mode using titania P-25 (surface area 50 m^2/g) as a photocatalyst and sodium hypochlorite as an oxidant for 5 h. The effect of operational parameters viz. catalyst dose, pH and oxidant concentration on the effectiveness of photocatalytic degradation was examined by using response surface methodology. The catalyst amount (0.25 g/l-1.25 g/l), pH (2-6) and oxidant concentration (3.06×10^{-6} M-15.3×10^{-6} M) were at the same time varied. The optimal values of operational parameters leading to 4-CP abatement were obtained by using response surface methodology. The percent degradation and COD reduction of 4-CP was found to increase with increases in the catalyst dose.

Vaez et al, (2012) reported to establish a quadratic model as a functional relationship between the efficiency of Acid Red 73 degradation (response) using immobilized TiO_2 nanoparticles and four independent variables. Four experimental parameters were chosen as independent variables: pH, initial dye concentration, H_2O_2 concentration, and anion concentration. The degradation efficiency was significantly affected by the initial dye concentration and the pH. The optimal values of the parameters were found to be a pH of 3, an initial dye concentration of 25 mg/l, an H_2O_2 concentration of 0.5 mg/l, and an anion concentration of 0.69 mg/l. The degradation efficiency approached 92.24% under optimal conditions. Regression analysis with an R^2 value of 0.9785 indicated a satisfactory correlation between the experimental data and predicted values

2.4 Technological gaps

Even though the heterogeneous and homogeneous photocatalytic processes has been extensively recognized for the degradation recalcitrant compounds, still literature on this aspect reveals the following technological gaps:

- Further research is needed to make the process cost and energy effective for its industrial applicability.
- Optimization of various parameters using response surface methodology still remains to be explored properly.
- There are limited reports on the degradation PCP using photocatalyst and the efficacy of photocatalyst in the presence of solar light is limited.

Keeping in view all these factors, an attempt has been made to obtain optimal settings of process parameters which may yield optimum degradation of model compound pentachlorophenol. Response surface methodology is being used to analyze as well as to plan the experiments. Further, study also being expanded to investigate photocatalytic degradation under UV and solar light using Zinc oxide (ZnO) and Titanium oxide (TiO_2).

2.5 Objectives of the present study

The study was undertaken with the following objectives:

- Photocatalytic degradation of the model compound Pentachlorophenol (PCP), a persistent non-biodegradable pollutant.
- Investigation of the effect of operating parameters such as catalyst dose, pH, light source (UV/solar) on the degradation efficiency of PCP.
- Optimization of the photocatalytic process parameters by applying Box Behnken design of response surface methodology (RSM).

CHAPTER 3

MATERIALS & METHODS

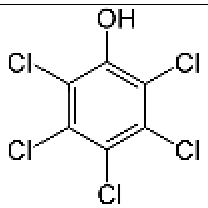
This chapter illustrates the materials and methods used during the study, including the chemicals, glasswares, instruments and equipments, procedures and BBD design used to degrade the model compound (PCP) with the UV/ZnO and UV/ TiO_2 catalysis. The collection of the varying photocatalytic conditions like pH, ZnO and TiO_2 dosages and oxidant dose for the degradation of pentachlorophenol with constant concentration (25 mg/l) make up the experimental matrix.

3.1 Materials

3.1.1 Pentachlorophenol (PCP)

Pentachlorophenol (PCP) having CAS number 87-86-5 was purchased from Sigma Aldrich (USA). Pentachlorophenol solution was used without further purification.

Table 3.1 Physico-chemical properties of Pentachlorophenol

Common name	**Pentachlorophenol (C_6HCl_5O)**
IUPAC name	2,3,4,5,6-Pentachlorophenol
Appearance	White crystalline solid
Boiling point	309–310 °C
Melting point	190–191 °C
Density (at 20°C)	1.978 g/cm^3 at 22 °C
Molecular weight	266.34 g mol^{-1}
Solubility in water (20°C)	0.020 g/L at 30 °C(insoluble)
Structure	

3.1.2 Photocatalysts

The photocatalyst used in the study were TiO_2 and ZnO. Titania P-25 (surface area 50 m^2/g and average particle size 30 nm) was obtained from Degussa, Germany and used as received. ZnO (5m^2/g) was purchased from Merck, Germany and used as such.

3.1.3 Chemicals

Different normality of 0.1 to 1 N HCl and 0.1 to 1 NaOH were used for adjustment of pH of the PCP solution. All the experiments were performed with distilled water.

3.2 Instruments and Equipments

3.2.1 Photoreactor

For photocatalytic treatment, UV reactor was used which is rectangular having dimensions of 4.5 × 3 × 3.5 and was made up of cast iron. Roof of the reactor was made up of wood having seven UV tubes (36 Watt each) attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Two magnetic stirrers were fitted in the reactor to carry out the photocatalytic reaction in slurry mode. The photoreactor at the lab level during the photocatalytic treatment is shown in Fig 3.1.

Fig 3.1 Photo reactor at lab level during photocatalytic treatment

3.2.2 Magnetic stirrer with Reaction vessel

Magnetic stirrer was used to conduct experiments in UV reaction to keep the mixture in suspension mode. Photocatalytic degradation was carried out in reaction vessels in the UV reactor/ chamber. Glass vessels were used for the photocatalytic reactions having a capacity of 1 L. The experiments were conducted in batch mode.

3.2.3 Air spargers

Air spargers were used to supply air continuously during the experiments in UV reactor as well as the solar experiments in order to oxidize the organic matter.

3.2.4 Syringe Filters

After photocatalytic treatment by UV photoreactor, the solution was filtered through syringe filters having millipore filters of 0.45 μm pore size.

3.2.5 Radiometer

Intensity of ultraviolet light and solar light was measured with the help of radiometer (Eppley, USA).

3.2.6 pH meter

A digital desktop, pH Meter (CP 901) from Century Instrument Company was used to measure the pH of the solution. Freshly prepared buffer solutions (of pH 4 and 9) were used to calibrate the instrument from time to time throughout the research.

3.2.7 Spectrophotometer

The spectrum was taken with UV-Vis Spectrophotometer (LABINDIA, UV – 3200 double beam spectro). The degradation studies were conducted by measuring absorbance in UV-Vis spectrophotometer, having a wavelength range from 190-1100 nm using a 1 cm quartz cell. All the experiments reported were carried out in a 4 ml quartz cuvette. The scan speed is 200 nm /min with a step of 1.0 nm. Wavelength resolution is 0.1 nm.

3.3 Software

Statistical software, Design-Expert 6.0 was used to generate the statistical and response plots, BBD design methodology was used.

3.4 Methods

3.4.1 Preparation of PCP solution

The concentration of PCP stock solution was in this present study was 25 mg/l. PCP compound solution of 25mg/l concentration was first prepared by dissolving 25 mg with 2 ml of 100% ethanol due to its lesser solubility in water and to make the solution quantity to 1 L, distilled water is used

3.4.2 Adsorption experiments

The adsorption experiment was performed in order to evaluate the adsorption of model compound (PCP) on the photocatalyst surface. The test was achieved using 100 ml aqueous solution of model compound in contact with optimum quantity of photocatalyst and kept in dark at room temperature then the solution was filtered through 0.45 µm filter and concentration of the unabsorbed was measured to find the extent of adsorption.

3.4.3 Slurry mode experiment

The photocatlytic experiments were achieved in specially designed reaction vessels. For the slurry mode experiments, photocatalyst in the form of powder was added to a solution which is to be degraded and the solution were kept under constant stirring using magnetic stirrers and aeration was carried out with the help of traditional aerator. The ambient temperature of the reaction vessel and UV chamber was maintained by exhaust. The concentration of PCP stock solution was used in this present study was 25 mg/l. For the degradation of model compound (PCP), photocatalytic experiments were performed by adding fixed amount of photocatalyst (TiO_2 and ZnO) in slurry mode to1000 ml of 25 mg/l of solution of pentachlorophenol in each trial at definite pH.

3.4.4 UV / Solar light irradiation

The aqueous suspension was subjected to irradiation under UV/solar light for fixed interval of time. The aqueous suspension was magnetically stirred.

3.4.5 Determination of degradation efficiency (%)

The degradation of the model compound was evaluated by monitoring absorbance as a function of irradiation time using spectrophotometer. At different time intervals sample was taken out with the help of syringe and then filtered through Millipore syringe filter of 0.45 µm. The absorption spectra were recorded at λ_{max} (219 nm). The degradation efficiency was calculated as follows:

$$\% \text{ Degradation} = 100 \times (C_0 - C)/C_0$$

Where C_0 = initial concentration of solution and C = concentration of solution after photo irradiation. The experimental medium was extended by varying different parameters like the dosage of photocatalysts, pH of the solution, time and initial concentration of substrate.

3.4.6 Determination of Total Organic Carbon (TOC)

The degradation of pentachlorophenol was also expressed with reference to the decrease in total organic carbon (TOC) for the optimized conditions. TOC test for the samples were conducted by IIT, Roorkee using TOC Analyzer.

3.5 Box–Behnken design

This design was developed by Box and Behnken (1960). Box and Behnken suggested how to select points from the three-level factorial arrangement, which allows the efficient estimation of the first- and second-order coefficients of the mathematical model. The Box–Behnken design provides three levels design (−1, 0,+1) for fitting response surfaces (variables), which are equally spaced. The number of experiments required (N) is given by $N = 2k (k - 1) + C_0$, where *k* is the number of variables and C_0 is the number of central points. The design is represented in Fig- 3.2 as a cube and all points lie on a sphere of radius $\sqrt{2}$. In addition, this design does not contain any points at the vertices of the cubic region created by the upper and lower limits for each variable. Fig 3.2 represents the Box–Behnken design for three variable optimization with its 17 experimental points.

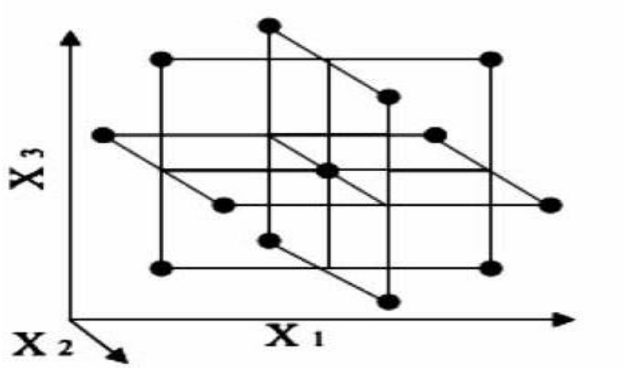


Fig 3.2 A Box–Behnken design for three factors (3^k)

This design is more economical and efficient in terms of the number of required runs than their corresponding 3^k designs with 27 experiments. Therefore, this design is useful in avoiding experiments that would be performed under extreme conditions, for which unsatisfactory results might occur. However, it is ineffective for situations in which we would like to know the responses at extremes.

In the present study, the three-level, three-factorial Box–Behnken experimental design was applied to investigate and validate photocatalytic process parameters. The following three independent parameters were chosen for study:

- CATALYST DOSE (A)
- pH (B)
- TIME (C)

The ranges of these factors were selected on the basis of preliminary experiments. Table 3.2 gives the levels of various parameters and their description. There are response parameter in the study is % degradation efficiency. In each test, degradation efficiency was calculated by change in the concentration of that component. 17 experiments were conducted according to the arrangement mentioned in Table3.2 of the next section. The Design expert 6.0 software was used for regression and graphical analysis of the data.

Table 3.2 Experimental design levels of chosen parameters

VARIABLES	**LEVELS**		
Coded level	Low(-1)	Middle(0)	High(+1)
A:Catalyst Dose (g/l)	0.20	0.35	0.50
B: pH	6.00	8.00	10.00
C: TIME(t)	2.00	4.00	6.00

CHAPTER 4

RESULTS & DISCUSSIONS

In the photocatalytic oxidation process, organic pollutants are degraded in the presence of photocatalysts (e.g. TiO_2, ZnO), an energetic light source and an oxidizing agent such as oxygen or air. This chapter presents the results of the photocatalytic degradation of pentachlorophenol (PCP) compound which was carried out using ZnO and TiO_2 catalysts. A matrix of experimental variables was developed in which the catalyst dose, pH, light source (UV/solar) were varied and applied to the model compound. Further experimental parameters are optimized with the help of software (Design expert).

4.1 UV –Vis spectra of Pentachlorophenol (PCP)

The degradation efficiency of PCP (25 mg/L) was recorded in terms of change in the intensity of characteristic peak at 219 nm. Fig-4.1 illustrates the UV-Vis Spectra of 25 mg/L of pentachlorophenol solution.

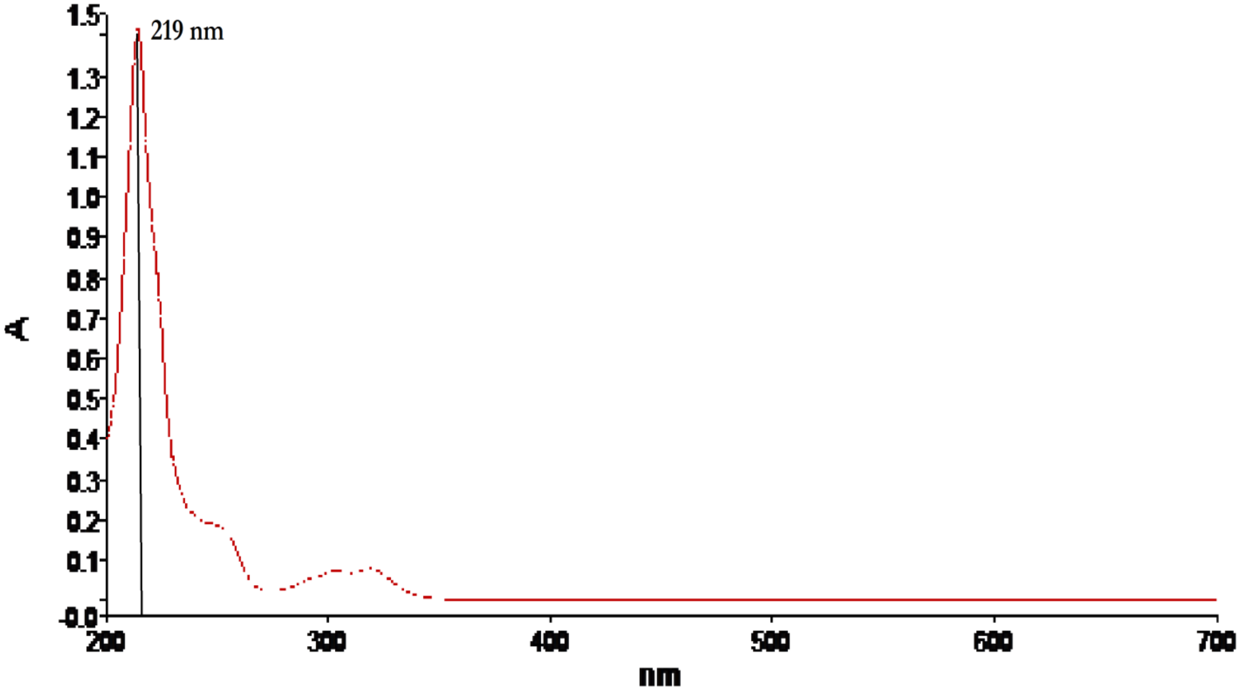


Fig 4.1 UV-Vis absorption pattern of pentachlorophenol

4.2 PRELIMINARY STUDIES

4.2.1 Photocatalytic degradation of PCP with TiO_2 as photocatalyst

The experiments were carried out, in order to assess the most favorable conditions for the photocatalystic degradation of PCP using TiO_2. In order to optimize the parameters preliminary studies were conducted by varying catalyst dose from .25 to 2 g/l for PCP of concentration 25 g/l at pH 8 under UV irradiation. The graph (Fig-4.2(a)) plotted between the amount of catalyst and degradation efficiency %.The maximum degradation efficiency was achieved at .5 g/l after 6 h of UV exposure. However, on further increasing the catalyst dose the degradation efficiency decreases.

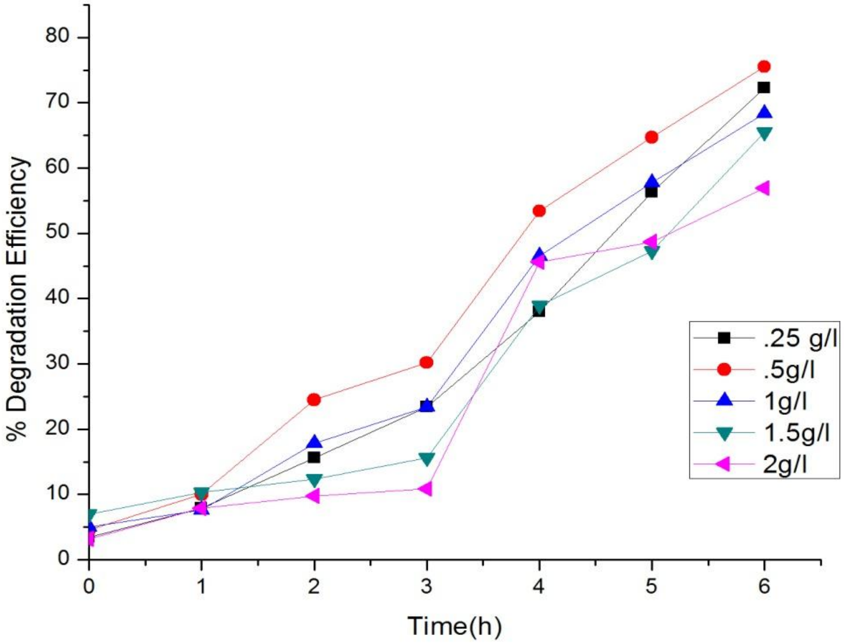


Fig 4.2 (a) Effect of Catalyst Dose on photocatalytic degradation of PCP with TiO_2 [pH]=8, [Conc.] = 25mg/l, [wavelength] = 219 nm, [IrridiationTime]= 6 h

Fig 4.2 (b) shows the effect of photocatalytic degradation of PCP with TiO_2. The maximum degradation was found to be with pH 8, catalyst dose 0.5 g/l.As the pH decrease the degradation efficiency also decreases. In acidic solution with the pH ZPC of 6.2, the positive surface charge of TiO_2 strongly attracted the negatively charged PCP (pKa = 4.74). As a result, the photocatalysis of PCP increased due to the increasing contact chance of PCP with hydroxyl radicals.

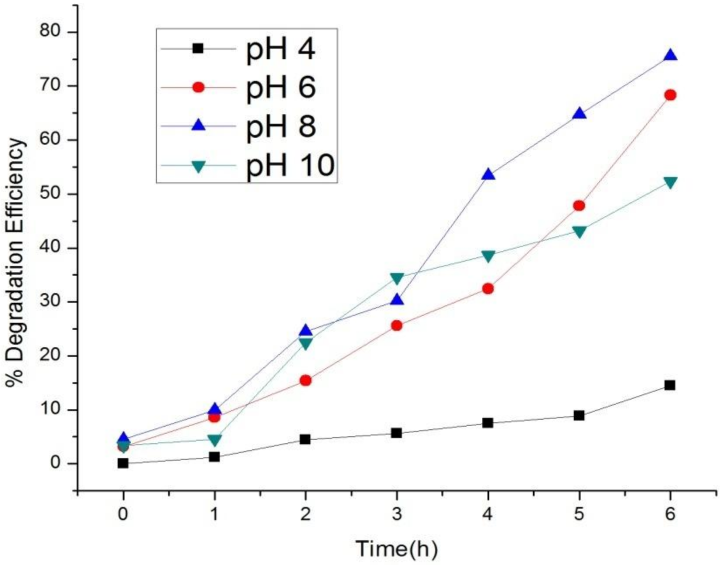


Fig 4.2(b) Effect of pH on photocatalytic degradation of PCP with TiO_2
[Catalyst Dose]=0.5 g/l, [Conc.] = 25mg/l, [wavelength] = 219 nm, [IrridiationTime]= 6 h

No data was recorded for the samples at pH 11 and 12 due to the low extraction recovery (only 3~ 4%) of PCP in strong basic solution because of its acid extractable property. Arcand et al, (1995) reported that the solubility of PCP in water increased drastically with increasing pH which reduced the extraction efficiency in strong basic solution.

The effect of light sources (UV/ Solar) were assessed on the degradation of PCP (25 g/l).The solar induced photocatalytic process in degradation of 74.3 % in comparison to 75.5 % degradation was achieved in UV light in Fig 4.2 (c).The results depict that UV light has better efficiency than solar light in the photocatalytic degradation of PCP .

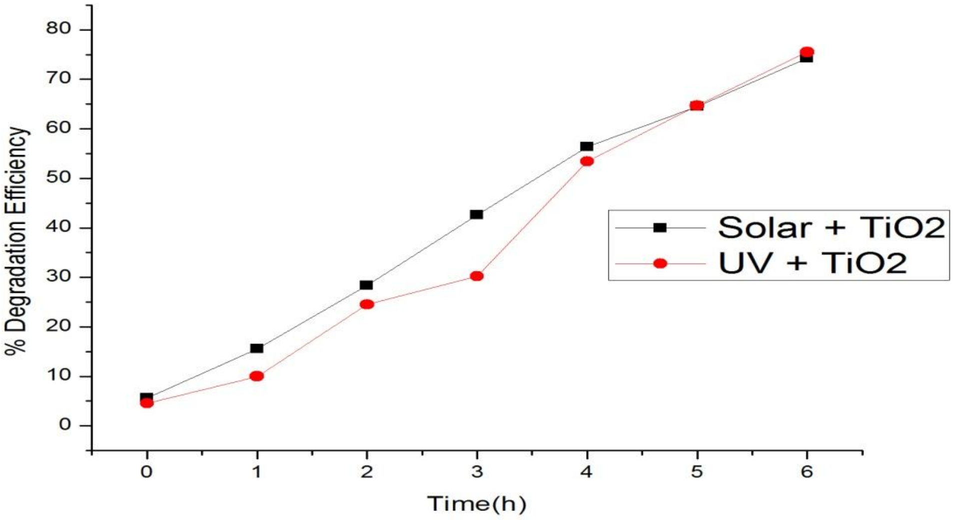


Fig 4.2(c) Effect of UV/Solar light on photocatalytic degradation of PCP with TiO_2 [Catalyst Dose]=0.5 g/l, [Conc.] = 25mg/l, [wavelength] = 219 nm, [IrridiationTime]= 6 h, pH=8

4.2.2 Photocatalytic degradation of PCP with ZnO as photocatalyst

The experiments were performed to optimize the parameters associated with the degradation of PCP using as ZnO catalyst under UV irradiation. The parameters considered were catalyst dose and pH. In order to optimize the parameters for the degradation of PCP (25 mg/l), preliminary studies for the photocatlytic experiments were performed by varying ZnO dose (.25 to 2 g/l) and pH (4 to 12). It has been suggested that the amount of catalyst plays a vital role in the degradation of organic compound so it it necessary to find the optimum loading for the efficient degradation so as to avoid excess photocatalyst in order to minimize the operational cost. The graph (Fig- 4.3 (a)) plotted between amount of catalyst and degradation efficiency %.The maximum degradation efficiency of 82.5% was obtained with ZnO dose (0.5 g/l) after 6 h of UV exposure. With further increase in catalyst dosage the degradation efficiency increases with catalyst dose of 2 g/l but decreases with 1.5 g/l at pH 8 and further increase in catalyst dose decreases the degradation efficiency. Thereafter, the degradation efficiency decreased with increase in catalyst loading which may be attributed to the fact that as the catalyst concentration increases, the turbidity of the solution increases which results in the decrease in the penetration of UV light due to light scattering [Akyol et. al., 2004].

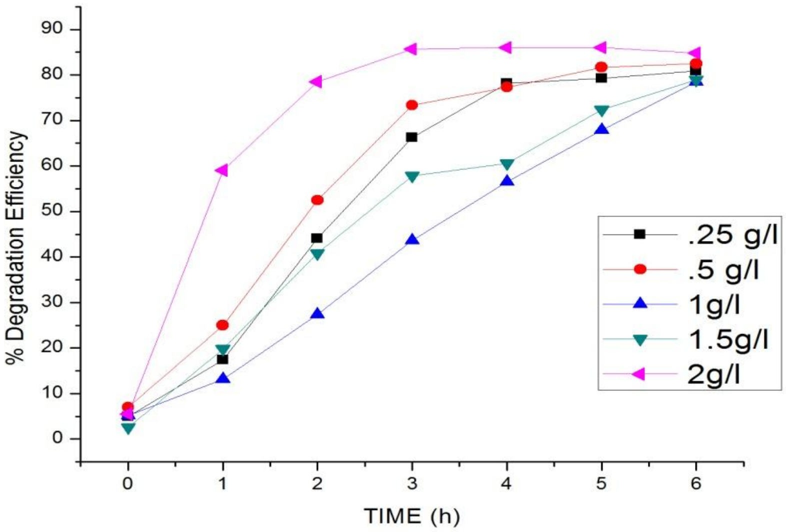


Fig 4.3(a) Effect of catalyst Dose on photocatalytic degradation of PCP with ZnO [pH] =8, [Conc.] = 25mg/l, [wavelength] = 219 nm, [Irradiation Time] = 6 h

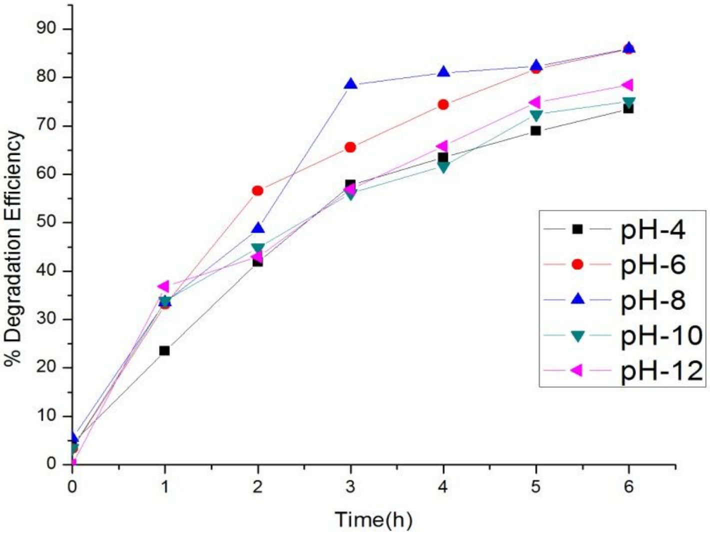


Fig 4.3(b) Effect of pH on photocatalytic degradation of PCP with ZnO [ZnO Dose]=0.5 g/l, [Conc.] = 25mg/l, [wavelength] = 219 nm, [IrridiationTime]= 6 h

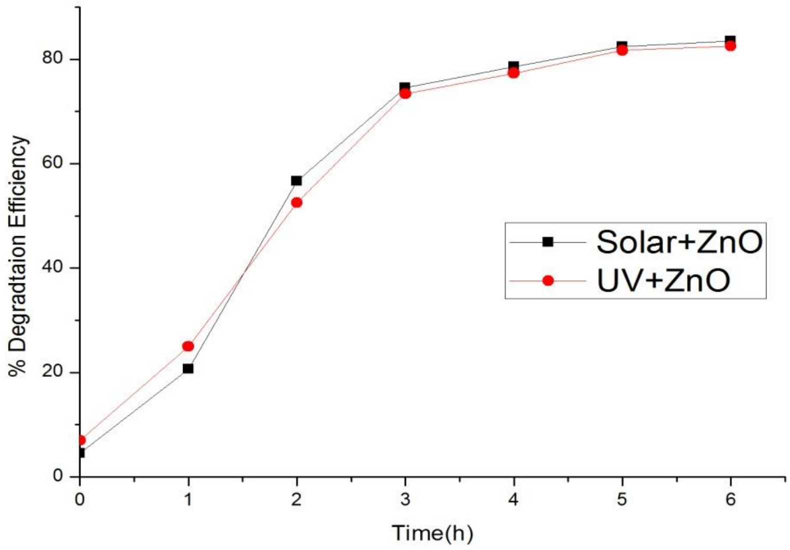


Fig 4.3(c) Effect of UV/ Solar light on photocatalytic degradation of PCP with ZnO [ZnO Dose]=0.5 g/l, [Conc.] = 25mg/l, [wavelength] = 219 nm, [Irradiation Time]= 6h,pH=8

However, Fig 4.3(b) reveals that the maximum degradation of 83.4 % was achieved with 0.5 g/l ZnO Dose at pH 8 after exposures of 6 h of UV irradiation. With decreasing catalyst dose to .25 g/l increase the degradation efficiency at very higher pace. Also, the aqueous suspension was exposed to solar light and UV in Fig 4.3(c). The degradation efficiency was found to be higher in solar light 83.45% as compared to 82.5 % that was attained in UV light shown in Fig 4.2.1. The zero point charge (zpc) for ZnO is 9.0 ± 0.3. ZnO surface is positively charged below pH 9 and above this pH, surface is negatively charged by adsorbed OH^- ions. The presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of $OH\cdot$ radical, which is widely accepted as principal oxidizing species resulting in enhancement of the efficiency of the process.

4.2.3 Adsorption studies of pentachlorophenol (PCP)

To understand the adsorption characteristics of PCP on catalyst surface experiment was carried out under UV/ZnO, UV/TiO_2, Dark/ ZnO and Dark/TiO_2. Fig 4.4 depicts the photocatalytic degradation of PCP under these conditions. The experiments were carried out under dark conditions using ZnO and TiO_2 to assess the adsorption of PCP on the surface of photocatalyst which was observed to be 30% and 11%, respectively. This degradation efficiency refers to adsorption of PCP on catalyst surface. Then the UV induced photocatalytic experiments were conducted using both the catalysts at substrate concentration of 25 mg/l and catalyst loading of .5 g/l. 82.5% degradation efficiency was achieved with in 6 h using ZnO whereas 75.5% degradation efficiency was observed using TiO_2 in the same duration.

This illustrates that ZnO shows better photocatalytic degradation of PCP.

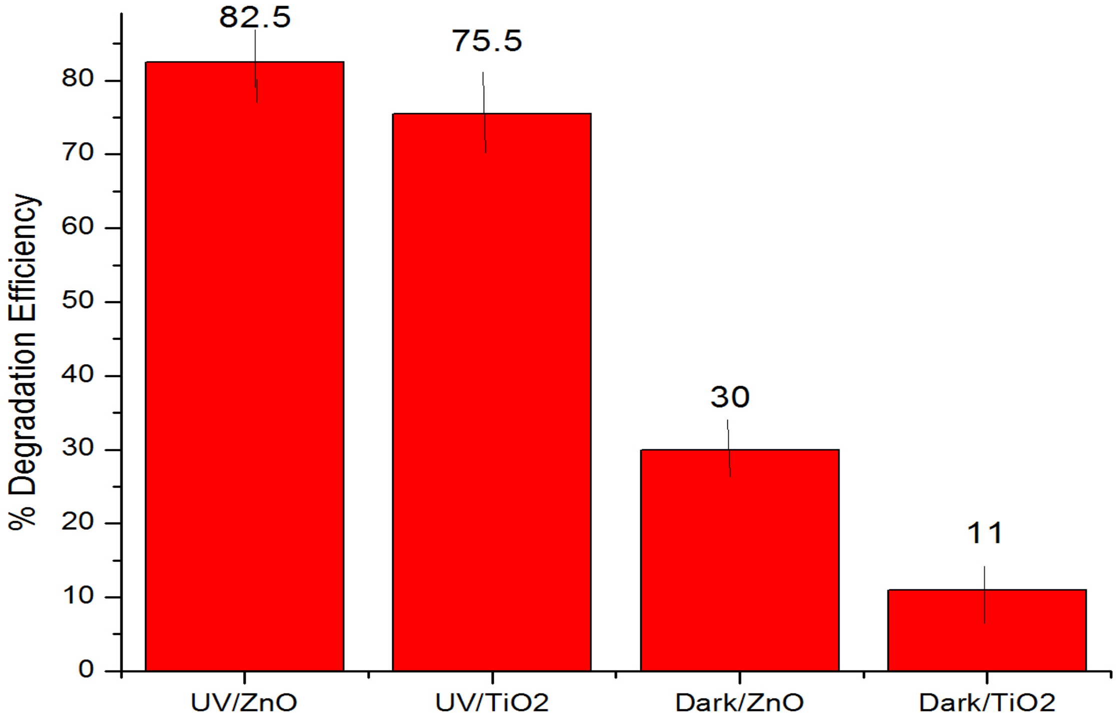


Fig 4.4Photocatalytic degradation of PCP under UV/Dark conditions [ZnO]=.5 g/l, [TiO_2] = .5 g/l, [Conc.] = 25 mg/l, [wavelength]= 219 nm, [Time]= 6 h

4.3 Optimization of the process parameters for the degradation of PCP

4.3.1 Model Fitting and Statistical Analysis

The experimental matrix design and the responses based on experiments proposed by Box Bhenken model and the results of each trial performed as per the experimental plan are shown in Table 4.1.

Table 4.1 The experimental values and measured response

Std	**Run**	**Block**	**Factor 1** A:Catalyst Dose	**Factor 2** B:PH	**Factor 3** C:t	**Response** Degradation efficiency
12	1	Block 1	0.35	10	6	82.1
3	2	Block 1	0.2	10	4	80.72
6	3	Block 1	0.5	8	2	25.4
7	4	Block 1	0.2	8	6	57.52
17	5	Block 1	0.35	8	4	74
2	6	Block 1	0.5	6	4	70.56
15	7	Block 1	0.35	8	4	75.6
5	8	Block 1	0.2	8	2	8.965
13	9	Block 1	0.35	8	4	74.6
9	10	Block 1	0.35	6	2	69.52
4	11	Block 1	0.5	10	4	71.92
8	12	Block 1	0.5	8	6	76.63
10	13	Block 1	0.35	10	2	46.31
1	14	Block 1	0.2	6	4	61.87
11	15	Block 1	0.35	6	6	81.32
16	16	Block 1	0.35	8	4	74
14	17	Block 1	0.35	8	4	76.1

The results were put into Design expert 6.0 software for further analysis. The fit summary of the output indicated that the quadratic model is statistically highly significant for degradation of PCP. Cubic model was not suggested as the Box–Behnken matrix has sufficient data to recognize the outcome of the present system. To decide about the adequacy of model for PCP degradation by photocatalysis, three different tests viz., Sequential model Sum of Squares, Lack of Fit Tests and Model Summary Statistics were carried out in the present study as shown in Table 4.2. To evaluate the adequacy of the model, analysis of variance (ANOVA) was applied. The results of the quadratic model for degradation efficiency in the form of Analysis of Variance (ANOVA) are given in Table 4.3.

Table 4.2 Selection of adequate model for degradation of PCP

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	72102.82	1	72102.82			Suggested
Linear	2872.495	3	957.4983	3.292574	0.0548	
2FI	222.144	3	74.04799	0.208098	0.8885	
Quadratic	2827.973	3	942.6577	9.034816	0.0084	Suggested
Cubic	726.7208	3	242.2403	266.7844	< 0.0001	Aliased
Residual	3.632	4	0.908	_	_	
Total	78755.78	17	4632.693	_	_	

Table 4.2 (a) Lack of Fit Tests

Source	Sum of Squares	DF	Mean Square	F-Value	Prob > F	Remark
Linear	3776.838	9	419.6486	462.1681	< 0.0001	
2FI	3554.694	6	592.449	652.4768	< 0.0001	
Quadratic	726.7208	3	242.2403	266.7844	< 0.0001	Suggested
Cubic	0	0	_	_	_	Aliased
Pure Error	3.632	4	0.908	_	_	

Table 4.2(b) Model Summary Statistics						
Source	**Std. Dev.**	**R^2**	**Adj. R^2**	**Pre. R^2**	**PRESS**	**Remark**
Linear	17.05302	0.431762	0.30063	-0.12026	7453.082	
2FI	18.86353	0.465152	0.144243	-1.46025	16367.95	
Quadratic	10.21451	0.890221	0.749078	0.648575	11633.21	Suggested
Cubic	0.95289	0.999454	0.997816		+	Aliased

Table 4.3 Analysis of Variance (ANOVA) results for response surface quadratic model

Source	**Sum of Squares**	**DF**	**Mean Square**	**F -Value**	**Prob > F**	**Remark**
Model	5922.612	9	658.068	6.307192	0.0120	Significant
Catalyst Dose	156.9549	1	156.9549	1.50432	0.2597	
pH	0.61605	1	0.61605	0.005904	0.9409	
Time	2714.924	1	2714.924	26.02094	0.0014	
(Catalyst Dose)^2	1029.688	1	1029.688	9.868953	0.0163	
(pH)^2	610.9351	1	610.9351	5.855451	0.0461	
(Time)^2	1230.21	1	1230.21	11.79084	0.0109	
Catalyst Dose *pH	76.47503	1	76.47503	0.732968	0.4203	
Catalyst Dose *Time	1.788906	1	1.788906	0.017146	0.8995	
pH*Time	143.88	1	143.88	1.379005	0.2787	
Residual	730.3528	7	104.3361			
Lack of Fit	726.7208	3	242.2403	266.7844	< 0.0001	Significant
Pure Error	3.632	4	0.908			
Cor Total	6652.965	16				

Std.Dev.	**10.21451**	**R^2**	**0.890221**
Mean	**65.12559**	**Adj R^2**	**0.749078**
C.V.	**15.68432**	**Pred R^2**	**0.648575**
PRESS	**11633.21**	**Adeq. Precision**	**9.446839**

From the ANOVA of the empirical second order polynomial model, F value for the model is 6.307192, implying that the model is significant (at $p < 0.05$). There is only a 0.01% chance that the “model F value” could occur due to noise. In this case, pH and $(pH)^2$ are highly significant model terms, while model values greater than 0.10 indicated that the model terms were not significant. The "Lack of Fit F-value" of 266.7844 implies that the Lack of Fit is significant. There is only 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise. Significant lack of fit test is in support of the fitness of the model. The "Pred R-Squared" of 0.648575 is in reasonable agreement with the "Adj. R-Squared" of 0.749078, confirming good predictability of the model.“Adeq. Precision” measures the signal to noise ratio. A ratio greater than 4 is desirable. The experimental ratio of 9.446839 indicates an adequate signal. It means that the model can be used to navigate the design space. The final mathematical equation in terms of actual factors (confidence level above 95%) as determined by the Design Expert software is:

$$\textbf{Degradation efficiency \%} = +78.29847 + 623.7319 * \text{ZnO Dose} - 49.2175 * \text{pH} + 30.62198 * t - 695.028 * \text{ZnO}^2 + 3.011406 * \text{pH}^2 - 4.27328 * t^2 - 14.575 * \text{ZnO Dose} * \text{pH} + 2.229167 * \text{ZnO Dose} * t + 1.499375 * \text{pH} * t$$

Fig-4.5(a) exhibits the normal probability plot of the residuals for percentage degradation. It may be noticed that the residuals are falling on a straight line which means that the errors are normally distributed.

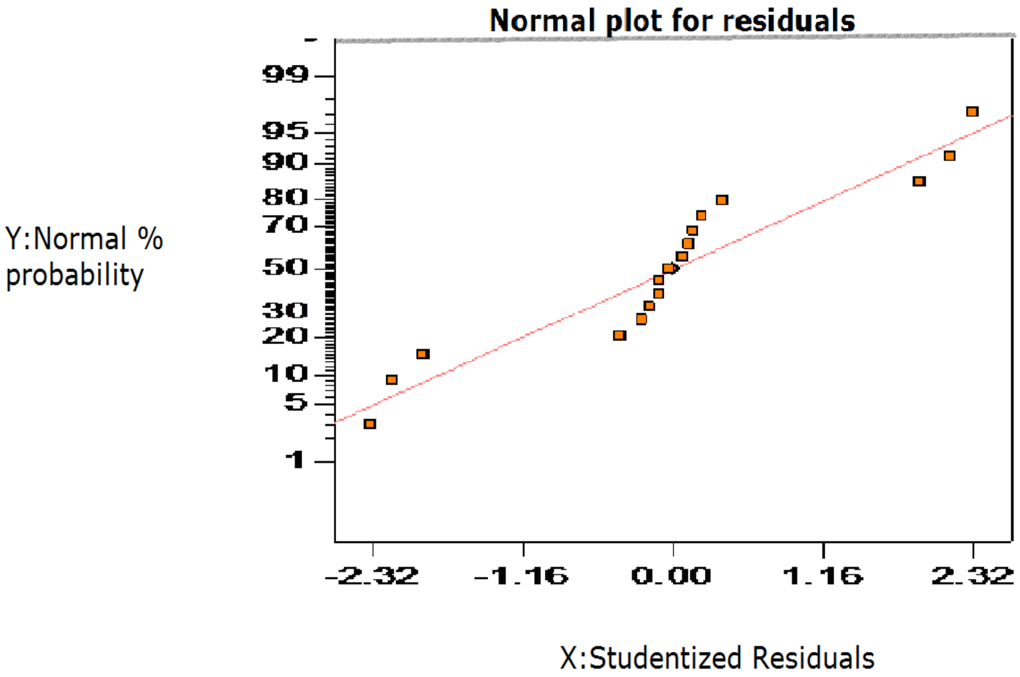


Fig- 4.5(a) Normal probability plot of the residuals for percentage degradation

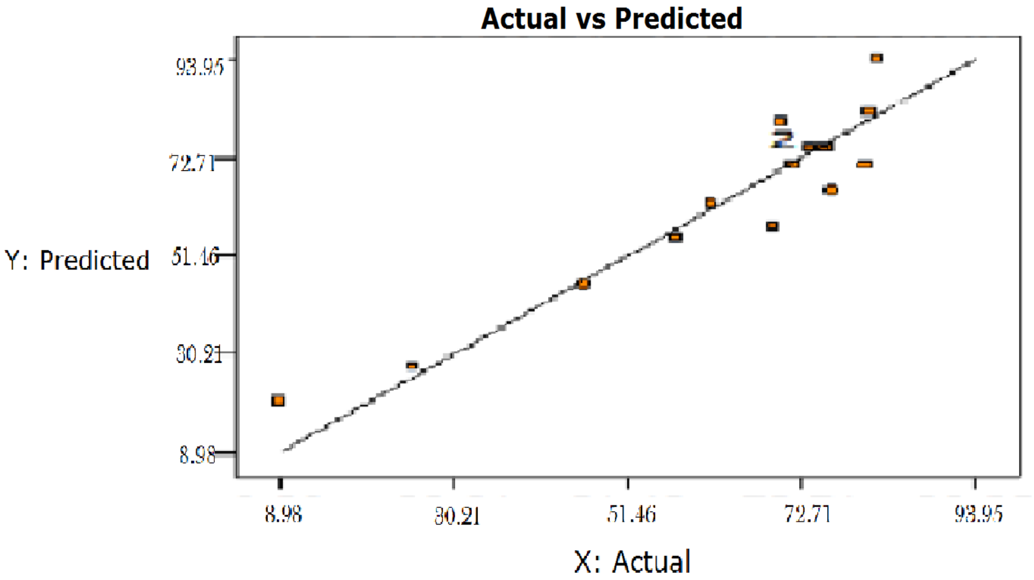


Fig – 4.5(b) Actual vs Predicted for degradation efficiency

4.3.2 Response surface analysis

Three-dimensional surfaces can be presented as graphical representations of the regression equation applied to determine the optimum values of variables and are widely used to achieve better understanding of the interactions between variables within the range considered

[Vildozo et al., 2010].The results of the interactions between the three independent variables and the response are shown in Fig 4.6 (a), 4.6 (b) and 4.6 (c). Fig 4.6 (a) illustrates the effect of ZnO dose and pH on the response (R) which is inversely related to the degradation efficiency of PCP. As pH is the highly significant factor, so maximum degradation was achieved at pH 9.5 and 0.35 g/l ZnO dose with minimum value of R.

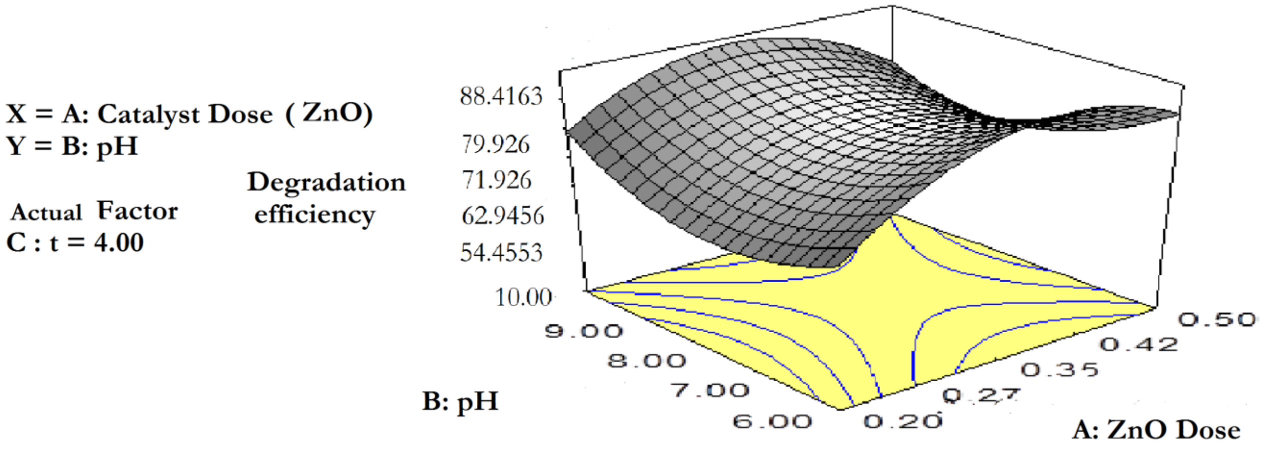


Fig - 4.6 (a) Effect of pH and ZnO dose on degradation efficiency of PCP
R= 1.0/Sqrt (%deg eff.), X= A: ZnO dose, Y= B: pH, Actual Factor C: t = 4.00 hrs

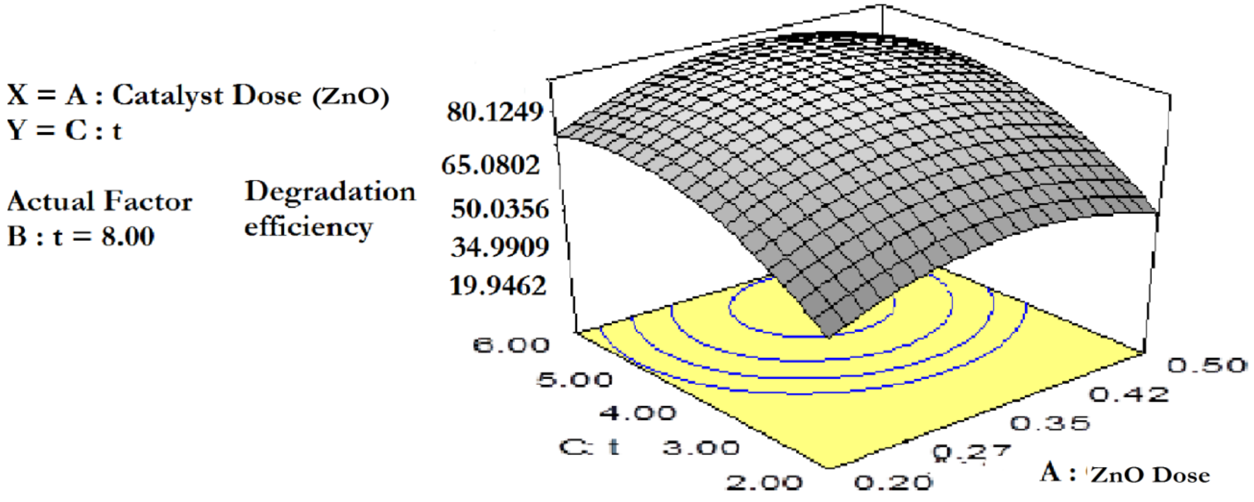


Fig- 4.6 (b) Effect of ZnO dose and time on degradation efficiency of PCP
R= 1.0/Sqrt (% deg eff.), X= A: ZnO dose, Y=C: t, Actual Factor B: pH=8.00

The effect of ZnO dose and time (t) on response (R) = 1.0/Sqrt (% deg eff.) is shown in Fig4.6 (b). As the ZnO dose and time (t) increases, the degradation efficiency increases and at 0.35g/l ZnO dose and time (t) at 5.2 hrs, R is minimum and the corresponding degradation efficiency is maximum. Fig 4.6(c) illustrates the effect of time (t) and pH on R=1.0/Sqrt (% deg eff.). It was found that degradation efficiency increases with increasing pH and time (t) and maximum degradation efficiency was achieved at pH 9.5 and time (t) at 5.2 hrs with minimum value of R and beyond that degradation efficiency decreases as R increases.

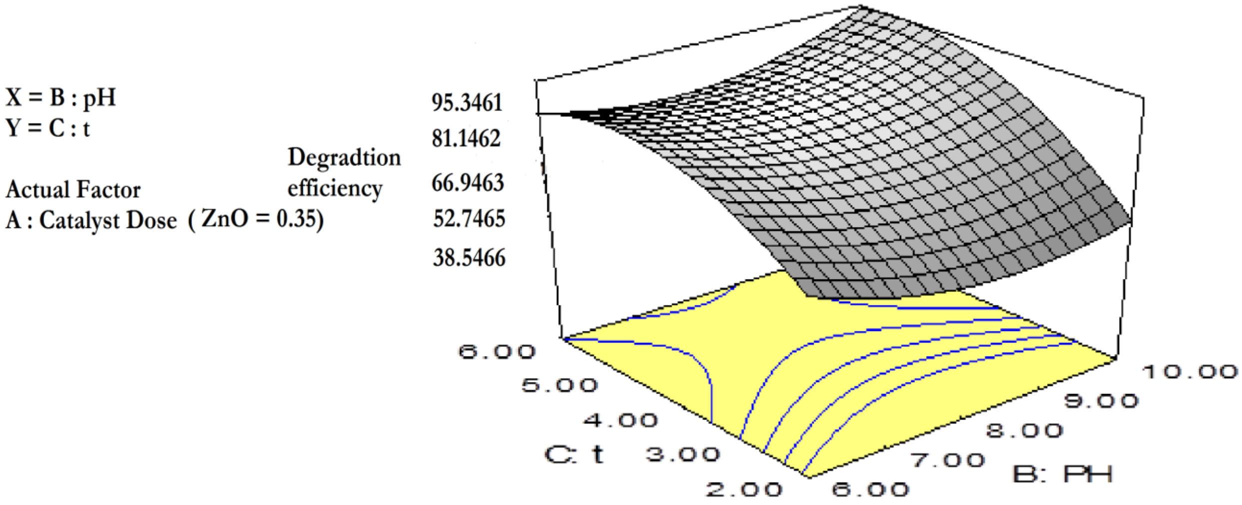


Fig- 4.6 (c) Effect of pH and t on degradation efficiency of PCP
R= 1.0/Sqrt (%deg eff.), X= B: pH, Y=C: t, Actual Factor B: ZnO dose= 0.35 g/l.

4.3.3 Model Validation and Confirmation

To confirm the adequacy of the model for predicting the maximum percentage degradation of PCP, a verification experiment was carried out using the optimum conditions. An average maximum degradation of 89.5 % was obtained, as shown in Table 4.3.3. The good agreement between the predicted value and the experimental value confirms the validity of the model for simulating the photocatalytic degradation of PCP.

Table 4.4 Optimum value of the process parameters for constraint conditions and their experimental values

		PCP Degradation (%)	
Variables	**Optimum values**	**Predictive**	**Experimental**
ZnO Dose (g/l)	**0.35**	**89.5%**	**89.5%**
pH	**9.5**		
Time (t, hrs)	**5.2**		

4.4 TOC Abatement Studies

A response surface methodology was applied to optimize the photocatalytic oxidation conditions total organic carbon (TOC) reduction as the target parameter to optimize, as related to the initial concentration of PCP (25 mg/l), ZnO Dose 0.5 g/l, pH 8 and as the control factors to be optimized. Maximal TOC removal (86.89%) was achieved when PCP samples were treated at pH 8 in the presence of ZnO dose.

CONCLUSION

Heterogeneous photocatalytic process has been proved to be proficient in the degradation of the persistent organic pollutants present in aqueous solutions. The observations clearly reveal the significance of choosing optimum process parameters to obtain high degradation rates which is most essential for practical applications of photocatalytic oxidation processes. In the present study, the photocatalytic oxidation of Pentachlorophenol, used in a variety of agricultural and industrial practices such as herbicides, insecticides, and fungicides as well as in the preservatives for timber, paints, and papers has been successfully achieved using ZnO and TiO_2. The effect of varying various parameters like catalyst dose, pH, UV/Solar irradiation and adsorption studies has been investigated. With 25 mg/l PCP concentration, ZnO dose was optimized to be 0.5 g/l, at operating pH 8.0 in 6 hrs time interval. In case of TiO_2, the optimized conditions were 0.5 g/l catalyst dose and pH 8.0 in 6 hrs time interval. 82.5% and 74.3% degradation efficiency has been observed with ZnO and TiO_2, respectively under the optimized conditions in 6 hrs of UV irradiation. The results clearly demonstrate that ZnO exhibits better photocatalytic activity as compared to TiO_2 in the photodegradation of PCP. The experiments were also carried out with solar light under optimized conditions (0.5 g/l ZnO, pH 8.0 at 6 hr and 1.5 g/l TiO_2, pH 8.0 at 6 hr) where 83.4% and 75.5% degradation efficiency was achieved after 6 hr of irradiation, which is same as achieved under UV irradiation. So, solar light can be efficiently used for the photocatalytic process, hence reducing the cost of operation. Box Behnken design based on response surface methodology has been applied to further optimize the conditions of PCP degradation using ZnO. Three independent variables were assigned as the factor limits, namely ZnO dose (0.5-3.0 g/l), pH (4-10) and time (4-6). The optimum conditions that yielded the maximum degradation efficiency of PCP (89.5%) were 0.35 g/l ZnO dose, pH 9.5 at 5.2 hr. The quadratic model fitted well with the experimental data with R_2 and R_2 adjusted correlation coefficients of 0.8978 and 0.7420, respectively and maximum TOC reduction 86.89% was achieved on optimized conditions (0.5 g/l ZnO dose, pH 8after 6 hrs). Hence, it can be concluded that photocatalytic process with solar light can be efficiently and cost effectively used for the degradation of PCP.

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